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## HIGH STRENGTH, HIGH TEMPERATURE POLYMERIC FIBERS

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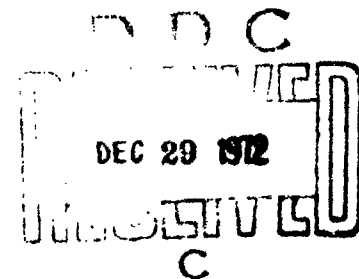
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## FOREWORD

This technical report was prepared by Whittaker Corporation, Research and Development Division, under US Air Force Contract No. F33615-70-C-1435. The work was administered under the direction of the Nonmetallic Materials Division, Air Force Materials Laboratory, with Mr. W. H. Gloor (AFML/MBC) as the Project Engineer.

This report covers the work conducted from 1 April 1970 to 1 July 1972. It is submitted in partial fulfillment of the contract and is catalogued by Research and Development Division as Report No. MJ0 3015.

This program was performed in the Polymer Research Department, under the direction of Dr. Walter P. Fitzgerald, Jr., Principal Investigator. Those assisting were Chadwick B. Delano, Senior Research Specialist, and R. Randolph Doyle, Research Chemist. Technician support was provided by William A. Tappen and Stephen Campbell, Research Technicians.

This report was submitted by the author in July 1972.

This technical report has been reviewed and is approved.



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## ABSTRACT

The subject program has been concerned with the synthesis of specifically ordered heterocyclic polymer systems for evaluation as high tenacity fiber candidates. Specifically sought in the performance spectrum of successful fibers was a high level of mechanical properties, high energy absorption (work-to-break) and high temperature performance. The primary structural criteria for polymer order are: chain growth which describes a straight line; the absence of bulky pendant groups; capability for approaching a planar structure and interchain bonding. These structural features, which are primarily responsible for providing enhanced thermal and mechanical capability relative to non-oriented counterparts, at the same time render the polymer system highly intractable. Hence, specialized solvent systems and dissolution techniques are required for wet spinnability.

The AF-Y-56 fiber has been generated by homopolymerization of 3,4-diaminobenzoic acid hydrochloride in polyphosphoric acid. The A-B polybenzimidazole has been obtained with inherent viscosities as high as 17.1 in sulfuric acid, reflecting an agglomerate macrostructure in solution. The polymer has displayed sufficient solubility in formic acid/m-cresol (80/20) for continuous multifilament wet spinning, with ethyl acetate as the preferred coagulant. The as-spun AF-Y-56 yarn, after 300°C drying has displayed tensile properties as high as: tenacity/elongation/initial modulus = 7.4 gpd/30%/97 gpd, with a tensile factor  $TE^{1/2} = 40$ , at a dpf = 0.5. This as-spun fiber displayed a moisture regain of ca. 25% at 70% RH.

A variety of heat-treatment schemes have been preliminarily investigated with the AF-Y-56 fiber to impart orientation and/or crystallization. Best results to date have been obtained with an on-the-run step drawing series, with a final exposure to 1000°-1050°C, with brief exposure. Such heat treatment has produced yarn with T/E/Mi = 13/2.2/501, with  $TE^{1/2} = 20$ . Initial modulus levels as high as 550 gpd have been obtained by such a strategy, by slight variation in time/temperature/tension.

Such heat-treated AF-Y-56 yarn retained ca. 77% of RT-tenacity at 600°F, ca. 53% at 700°F, and ca. 47% at 750°F, in initial testing.

Attempts were also made to prepare useful spinning solutions of the ladder BBL polymer system, derived from naphthalene tetracarboxylic acid (or its anhydride) and tetraminobenzene. Controlled condensation routes in dipolar aprotic solvents produced only low molecular weight polymer which did not produce useful fiber. Higher molecular weight BBL polymer, prepared in PPA, was found to be soluble to several percent in perfluoromethanesulfonic acid, but no useful fiber was produced in initial small-scale spinning studies.

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## SECTION I DISCUSSION OF RESULTS

### INTRODUCTION

The aromatic heterocyclic family of polymers is a most fruitful area for the development of a high-strength, high-modulus, thermally stable organic fiber system. The structural criteria for such an organic fiber impose several synthesis requirements on the systems involved. The systems deemed useful, according to these criteria, will generally fall into categories termed improcessable by virtue of intractability. As such, unique and/or specialized methods for their synthesis can be anticipated for fabrication.

The following structural criteria must be considered for a polymer to exhibit an abnormally high tensile strength and an abnormally high degree of stiffness. The primary concern is achieving an ultra-high degree of orientation (and crystallinity). A highly rigid system is required, with the polymer-growth describing an essentially straight line. It is not believed necessary for the repeating unit bond angles to describe a straight line, as in the case of poly-p-phenylene, as long as the overall chain growth describes a straight line. The polymer chain structure must be essentially planar for optimum packing. This requirement virtually limits consideration to all-aromatic structures, devoid of bulky or rotation-free side groups. Another prime criterion is high degree of very efficient interchain hydrogen-bonding to provide additional longitudinal and rotational rigidity, at the same time providing for an increased molecular density. In an all-aromatic system, these effects would be augmented by a high degree of interchain ring- $\pi$ -orbital overlap.

It must be borne in mind that dilution of a requisite structural feature, for example, by partial isomer substitution has a catastrophic effect upon the overall order of the system, and the resultant fiber invariably possesses the properties expected of the unordered isomer. Consequently all our synthesis endeavors were directed at systems which embody these features.

In summary, the systems most capable of generating a liquid-crystalline solution and highly-ordered fiber in spinning are those systems which are straight and planar along the chain growth axis, and which are streamlined and constructed for most efficient interchain bonding. The approach to ultimate compaction into an essentially planar system can be carried out by final heat treatments in yarn form under tension "on-the-run."

## PROGRAM OBJECTIVES

The primary objective of this program has been the development of fibers and multifilament yarns exhibiting a high level of mechanical properties, high energy absorption and high temperature performance superior to present materials. These fibers are needed for such applications as high temperature decelerators. In addition, nonflammable and nonmelting fibers upon exposure to high thermal fluxes would be most desirable. Target tensile properties are: tenacity/initial modulus = 20 gpd/1300 gpd at a density less than 1.6 g/cm<sup>2</sup> with thermal retention of 50% of room temperature tenacity at 1400°F (1 min) and 75% of same after 250 hours at 750°F. The suitability of the fiber and yarns for carbonization and graphitization has been a secondary, longer range objective.

## DISCUSSION OF RESULTS

Overall program efforts were largely concerned with controlled synthesis routes to several ordered polymer systems treated separately below. In all cases, the criteria for an ordered system, discussed above, have been followed in selection of candidate systems.

### A. The AF-Y-56<sup>\*</sup> System

The bulk of the effort on this program has been directed toward the most promising AF-Y-56 polymer system, an A-B polybenzimidazole, whose chain-growth axis describes a straight line, and whose structure displays the requisite features for order, both in solution and in shear-fabricated form.

The most ready access to the AF-Y-56 polymer has been based on a modification of the original procedure of Dawans and Marvel,<sup>(1)</sup> using the PPA-polymerization of the hydrochloride of 3,4-diaminobenzoic acid (DABA). Two synthesis approaches to obtaining the title ordered polymer system, I, were investigated, as shown in Figure 1.

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\* AF-Y-56/Air Force Yarn from Poly-2,5(6)benzimidazole.

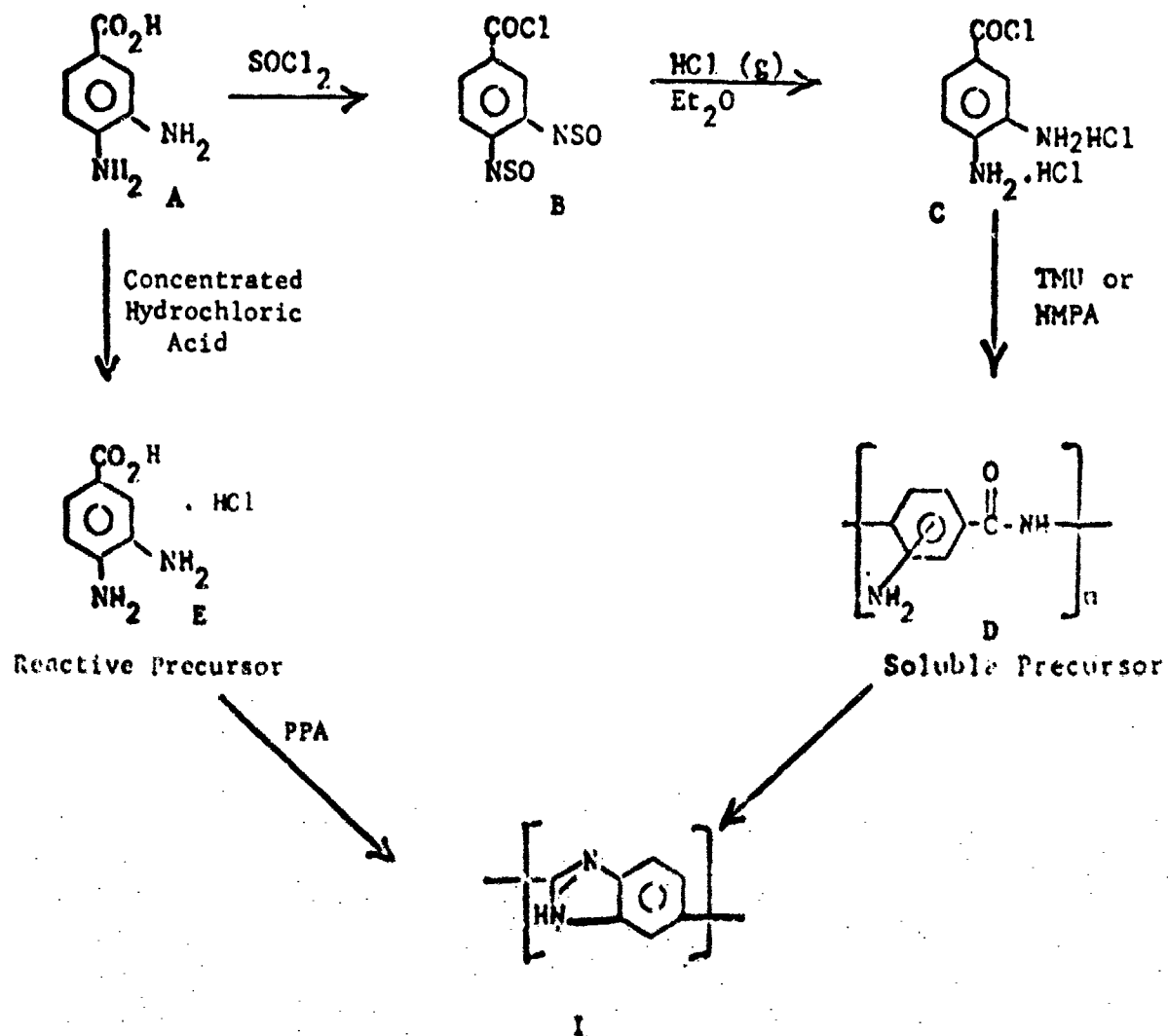


Figure 1. AF-R-56 Synthesis

\* R = Resin

As seen from Figure 1, 3,4-bis-thioniminobenzoyl chloride, B, isolated as a yellow crystalline solid by flash distillation of the crude product from the reaction of recrystallized 3,4-diaminobenzoic acid with excess refluxing thionyl chloride, was converted to the A-B monomer, 3-4-diaminobenzoyl chloride hydrochloride C by ethereal hydrogen chloride treatment. This latter A-B monomer showed a persistent reluctance to polymerize to a high molecular-weight PBI in either DMAC or TMU solvent. Termination occurred at an inherent viscosity ( $\eta_{inh} \leq 0.4$ )\* which is considerably below the threshold of useful spinnability. All polymer solutions were completely isotropic, in contrast to the anisotropic methane-sulfonic acid solutions of the high-inherent polymer prepared in PPA. The purity of the A-B monomer C was suspect since purification was limited to washing the reactive solid with non-polar solvents.

In marked contrast to the above, the PPA-approach to the polymer resulted in ready attainment of polymer with an inherent viscosity in excess of 9.0 (0.5%  $H_2SO_4$ ). Method variations employed to obtain high M.W. polymer by this route and the operations carried out upon the resulting isolated polymer are discussed under the separate headings below.

#### 1. Monomer Purification

In order to optimize the molecular weight development of the AF-Y-56 polymer, efforts were directed toward purification and quality control of the requisite A-B monomer, 3,4-diaminobenzoic acid (DABA). These efforts included the evaluation of several basic approaches to the purification, involving acid-base reactions, recrystallizations, and isolation of acid salts of the monomer such as the hydrochloride or phosphate. Some effort was also expended on determining the nature and quantity of the impurities. The results of these efforts are tabulated below:

- (1) The melting behavior of 3,4-diaminobenzoic acid (DABA) fails to provide adequate indication of monomer purity, largely due to its rapid decarboxylation in the melt.
- (2) VPC analysis on the silylated DABA indicated less than 1% impurity corresponding to p-aminobenzoic acid in the as-received DABA (Aldrich).

\* 0.5%/H<sub>2</sub>SO<sub>4</sub>

- (3) TLC verified the virtual absence of this impurity from the Aldrich DABA, but did show trace amounts present in the Hoechst DABA.
- (4) Polarography showed the presence of at least one easily reducible organic compound, present in ca. 1% amounts (Aldrich DABA), but the results were not conclusive as to the nature of the impurity (i.e., nitro, azo, quinone diimine, etc.). Assuming a two-electron change to the reduced form, the quantity of this impurity detected probably eliminates 3-nitro-4-aminobenzoic acid as a major impurity.
- (5) Neutralization equivalents failed to correlate well with other indications of purity for DABA recrystallized from de-oxygenated water. Thus, results obtained with 3,4-diaminobenzoic acid samples from the three available sources of this monomer gave the following results:

	<u>Melting Point (corrected)</u>	<u>Equivalent Weight</u>
Aldrich (as received) (97%)*	207°C	152
American Hoechst (99%)*	206.5°C	152
Aldrich (crystallized from H <sub>2</sub> O)	215.5°C	150

(Theory for the monomer is 152)

It is unlikely that monomer purity was decreased during purification from water. It is rather suspected that a higher molecular weight impurity was removed by the water purification and that this last entry is actually the purest monomer.

- (6) Conversion of the Aldrich and Hoechst materials to their respective hydrochlorides gave the following total acidity values (theory for the dihydrochloride, its hydrate, the

<u>Source</u>	<u>Ether, Dioxane Extracted Vacuum Dried</u>	<u>Dried Overnight @ 110°C</u>
Aldrich	78.0	94.7
American Hoechst	86.7	91.7
Combined Hoechst & Aldrich		94.11, 94.14

\* Suppliers purity minimum.

monohydrochloride and its hydrate are 75.0, 81.0, 94.3, and 103.3, respectively). It is quite evident that the 3,4-diaminobenzidine acid forms a stable monohydrochloride. (2) This result agrees with those obtained by von H. Salkowski except that in this case isolation was via the monohydrochloride as a monohydrate. These results were most promising for both the purification and quality control of the monomer, and this route was selected as the best found on the program.

- (7) Pilot polymerizations conducted in PPA for the purpose of monomer quality control demonstrated that monomer purity was not as critical in obtaining high molecular weight AF-R-56 as were the conditions used in the polymerization itself. This unexpected result which is discussed in detail in the following section, largely influenced the decision to de-emphasize further monomer purification attempts to reach a higher purity than that obtained with the monomer hydrochloride.

Upon selection of Route No. 6 described above as the method of choice to obtain pure monomer, ten-pound lots of the monomer were obtained from the American Hoechst Corporation. The purification of this material by the described method produced monomer with a slight pink color. After drying at 110°C (18 hours) the resulting crystals had a light tan color.

In lieu of additional efforts to improve the existing purification method the addition of a few percent of sodium hydrosulfite was employed. This reducing agent was added to the solution of DABA.HCl after its treatment with charcoal prior to the addition of concentrated hydrochloric acid. The resulting crystals were visually free of the pink color, and only a slight tan coloration was observed upon their drying at 110°C (18 hours).

Another modification to the procedure was made at this point. The crystals, as isolated from the acid solution, were washed with ether to remove excess water and hydrochloric acid and then vacuum dried at room temperature. This modification produced white crystalline DABA: total acidity 94.5, 94.8 (Theory 94.3).

In summary, it appears that some batch-to-batch variation in monomer purity may be expected, and further efforts in this area may be needed as new lots are obtained from the manufacturer. No significant variation in total acidity determinations was obtained in three purifications of this material as shown below.



### Total Acidity Determinations:

#### Purification of Hoechst 3,4-Diaminobenzoic Acid

<u>Purification Reference</u>	<u>Total Acidity</u>
RRD 2201-9-B1	95.0, 95.4
RRD 2201-9-B3	95.0, 94.3
RRD 2201-9-B4 (ether washed)	94.5, 94.8

## 2. Polymerization Studies

In the optimized procedure developed on this program, the above DABA.HCl monomer is polymerized in PPA according to the following procedure: thus, a 2.0%-solids solution of 240 g of DABA.HCl in 83.05% polyphosphoric acid is polymerized for 2 hr at 180°C, followed by 4 hr at 200°C, followed by a final 18 hours at 220°C, all without stirring. The polymer is precipitated in water in a blender, isolated by filtration, and extracted successively with boiling water (72 hr), ammonium hydroxide (18 hr), and water, and dried to constant weight. A yield of ca. 140 g of AF-R-56 is obtained, which displayed inherent viscosity as high as:  $\eta_{inh} = 17.1$  at 0.005% in H<sub>2</sub>SO<sub>4</sub>. Routinely the range of inherent viscosity obtained from this procedure is 10-16.

Table I lists selected polymerization of purified DABA.HCl in PPA, illustrating the effect of reaction conditions on inherent viscosity development.

### a. Polymer Characterization

Early in the program a study was carried out to elucidate the structure of the polymer as produced in PPA, specifically with respect to the true significance (residual hydration or uncyclized amino-amide) of the residual oxygen found to be present in the polymer. Table II lists the results of this study. Included in the table are the final polymerization temperatures, the weight loss of the polymer after its standardized 24 hour drying at 110°C, and subsequent vacuum-heating to 300°C in N<sub>2</sub>, and also the oxygen and phosphorus contents. The P<sub>2</sub>O<sub>5</sub> content of the polymerizing medium for these studies was standardized, to remove this variable.

The varying oxygen contents of the polymers seen in Table II indicates that the 4-hour at 300°C/1 mm Hg is an insufficient drying schedule to entirely remove the water from the polymer. The presence of residual uncyclized amino-amide linkages in the polymer is a less likely alternative, because of the magnitude of the residual oxygen values in some instances. Because of the stringent processing, it is highly unlikely, with a theoretical oxygen value of 11.9% for a 100% amino-amide structure, that the values of 7.0% and 7.9% obtained in two cases, could be due to uncyclized residues.

TABLE I

## A-B PBI PREPARATION IN POLYPHOSPHORIC ACID

<u>Notebook Reference</u>	<u>Monomer Neutral Eq.*</u>	<u>P2O5 Content of the PPA</u>	<u>Reaction Schedule</u>	<u><math>\eta_{inh}</math> (0.5% H<sub>2</sub>SO<sub>4</sub>)</u>
02201-15-B1	94.04	--	4 hr @ 180°C 2 hr @ 200°C 5 hr @ 220°C	7.82
02201-27-B1	--	83.05	2 hr @ 180°C 4 hr @ 200°C 18 hr @ 220°C	9.66;10.00
02217-4-B9	94.25	83.1	2 hr @ 180°C 4.5 hr @ 200°C 17.5 hr @ 220°C 2 hr @ 240°C	5.30
02217-12-A8	93.73	83.0	3 hr @ 180°C 22.5 hr @ 200°C 4 hr @ 240°C	7.96;8.41
02217-9-B7	94.22	83.1	2 hr @ 180°C 4 hr @ 200°C 18 hr @ 220°C	8.06
02217-33-B9	94.38	83.15	2 hr @ 180°C 4 hr @ 200°C 18 hr @ 220°C	6.30
02217-39-B5		83.5		9.76
02217-44-B7		83.5		9.32

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\* Theory = 94.3

TABLE II

## FINAL AF-R-56 CHARACTERIZATION

Notebook Reference	Reaction Temperatures	TGA Wt. Loss (H <sub>2</sub> O), %	% O*	% P*
2217-4-B9	17.5 hr @ 220°C 2 hr @ 240°C	22	7.00	>0.01
2217-16-B12-1	23 hr @ 220°C	18	5.24	0.65
-2	↓	14	3.43	0.41
-3		16	2.64	0.012
-4		25	3.09	0.010
2217-16-B14-1	23 hr @ 220°C	21	3.58	0.003
-2	5 hr @ 240°C	20	2.35	0.005
-3	↓	12	1.72	0.008
-4		--	2.57	0.007
2217-9-B7	18 hr @ 220°C	10	3.31	0.006
2217-22-B7	↓	6	0.74	0.005
2217-25-B3-A		10	3.86	0.002
2217-29-B7		--	4.47	0.005
2217-35-B1	↓	--	7.94	0.09

\* Analysis carried out on polymer after heating 4 hr @ 300°C at less than 1 mm Hg.

As further evidence, it is known that caustic (pH >13) can effect ring closure of the amino-amide linkage, to imidazole. The workup conditions of the AF-R-56 polymer with refluxing concentrated ammonium hydroxide would be expected to also contribute similarly to supplemental closure of residual amino-amide linkages, although this postulate has not yet been established.

With the attainment of very low residual phosphorus content (0.004%) in the AF-R-56 polymer, direct analysis for oxygen was made possible. Such analysis was highly desirable to permit an assay of extent of ring-closure, since the fully-cyclized PBI structure contains no oxygen. Residual amino amide linkages in small percentage are also suspect, despite lack of spectral evidence, due to the observed drop in inherent viscosity upon redissolution and re-precipitation. The analyses obtained are summarized in Table III.\*

\* Compare to elemental analyses obtained in Reference 3.

TABLE III

## ELEMENTAL ANALYSIS STUDIES WITH AF-R-56 SAMPLES

<u>Polymer Treatment or Condition</u>	<u>% C</u>	<u>% H</u>	<u>% N</u>	<u>% O</u>	<u>% P</u>	<u>% Ash</u>	<u>Total</u>
a) <u>Theoretical</u>							
Calculated for AF-R-56 (C <sub>7</sub> H <sub>4</sub> N <sub>2</sub> ) <sub>12</sub>	72.41	3.47	24.12	0.00	0.00	0.00	100.00
b) <u>Experimental</u>							
1. Polymer 2201-15-B1 Air dried 16 hr/110°C (5 hr cycle @ 220°C)	67.68	3.98	22.17	6.01	0.004	0.13	99.97
2. Dried #1 4 hr additional @ 300°C/2 mm	67.98	4.63	23.57	4.52	0.004	0.00	100.70
3. Polymer 2201-27-B1 Dried 4 hr @ 300°C/2 mm (18 hr cycle @ 220°C)				2.59	0.004		
4. Multifilament Fiber Dried 16 hr/110°C (5 hr cycle @ 220°C)	56.03	4.63	17.93	-	<0.05	*	

\* Sample contained 1.20% sulfur after H<sub>2</sub>SO<sub>4</sub> re-dissolution and spinning.

Sample No. 2201-23-B11B, prepared in a reaction with a 5-hour cycle at 220°C, and subsequently worked up to remove all but trace phosphorus (0.004%), as described previously, and finally dried for 16 hours at 110°C, showed an oxygen content of 6%. That this value may represent, at least partially, water of hydration is indicated by the fact that additional drying of the sample under more stringent conditions (4 hr @ 300°C/2 mm) reduced the oxygen content to 4.5%. This latter drying cycle is considered to be below the threshold of amino amide - benzimidazole cyclization.

On the other hand, some evidence has also been obtained for trace residual amino amide. It has been shown previously that extent of cyclization is correlatable with duration of the 220°C-polymerization cycle of PPA. As shown in Table III, the scrupulously dried polymer with 4.5% residual oxygen had been exposed to only 5 hr reaction time at 220°C. A similar purification and 300°C-vacuum drying scheme was used on a polymer sample which had been exposed to 18-hr at 220°C in the polymerization. This sample exhibited only 2.6% residual oxygen. This result

correlates well with the increases in inherent viscosity observed with longer reaction cycles at 220°C. It is felt that these rather subtle differences in structure among the various polymer samples are being reflected in the solubility differences and in the variable spinning behavior observed with these samples. With this analytical background, and with the detailed investigation of the PPA-polymerization of 3,4-diaminobenzoic acid that has been carried out, it became possible to stabilize the polymer purity and inherent viscosity for more uniform dope preparation for reproducible wet spinning performance.

The inherent viscosity values of several selected polymer batches were re-determined under conditions designed to more reliably preclude the possibility of interference by adventitious moisture entrainment. In addition, lower polymer concentrations were investigated to reduce the time required to perform each analysis (ca. eight hours at 0.5% solids with the very high inherents observed with this polymer).

Accordingly Table IV summarizes the results of this investigation, and Figure 2 shows the variation of inherent viscosity with polymer concentration. Included in Table IV are the tenacities obtained for the as-spun yarns from the respective polymers from formic/cresol with diethyl ether as coagulant. The table and the figure both show the anticipated increase in the inherent viscosity as the polymer concentration is reduced. Unexpected in Figure 2 is the apparent logarithmic dependence of the polymer inherent viscosity values upon its concentration. The reduced specific viscosity also shows a logarithmic dependence upon the concentration of the polymer. The intersection of these two extrapolations (usually not logarithmic) at zero concentration suggests an intrinsic viscosity of 15.5 dl/g.\*

Most striking in Table IV is the batch-to-batch reproducibility of the high inherent viscosities observed for the A-B PBI system. The values at 0.005% concentration are in excess of 10 dl/g in 6 out of 7 of the AB-PBI polymers. Until molecular weights of these polymers have been ultimately demonstrated, classical interpretation of these inherent viscosities will not be attempted.

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\* 0.005% / H<sub>2</sub>SO<sub>4</sub>

TABLE IV  
INHERENT VISCOSITIES OF AF-R-56 IN SULFURIC ACID

<u>Notebook Reference</u>	<u><math>\eta_{inh}</math> @ .5% Concentration</u>	<u><math>\eta_{inh}</math> @ 0.005% Concentration</u>	<u>Highest Observed Yarn Tenacity, gpd</u>
2217-12-A8	8.41*	11.45; 11.78	2.4
2217-33-B9	6.30*	9.80	1.8
2217-39-B5	9.76*	16.64	5.1
2217-44-B7	9.32*	14.51	3.4
2217-46-A10	11.68	14.44; 15.15	4.8
2217-50-A10	--	15.77	3.6
2225-3-A10	8.21	11.69	--

\* These inherents were obtained with nominal polymer drying precautions being exercised.

A fairly comprehensive investigation was made of useful solubility of reasonably high-inherent ( $\eta_{inh}$  - 7.8)\* AF-R-56 for wet spinning. Solvents were investigated both at room temperature, and also after prolonged reflux. In no case was there found to be any benefit obtained for the use of elevated temperatures to effect solubilization. Results for single solvents and solvent/salt pairs are summarized in Table V. The polymer had previously been purified to 40-ppm residual phosphorus by the procedure discussed above.

\* 0.5%/H<sub>2</sub>SO<sub>4</sub>

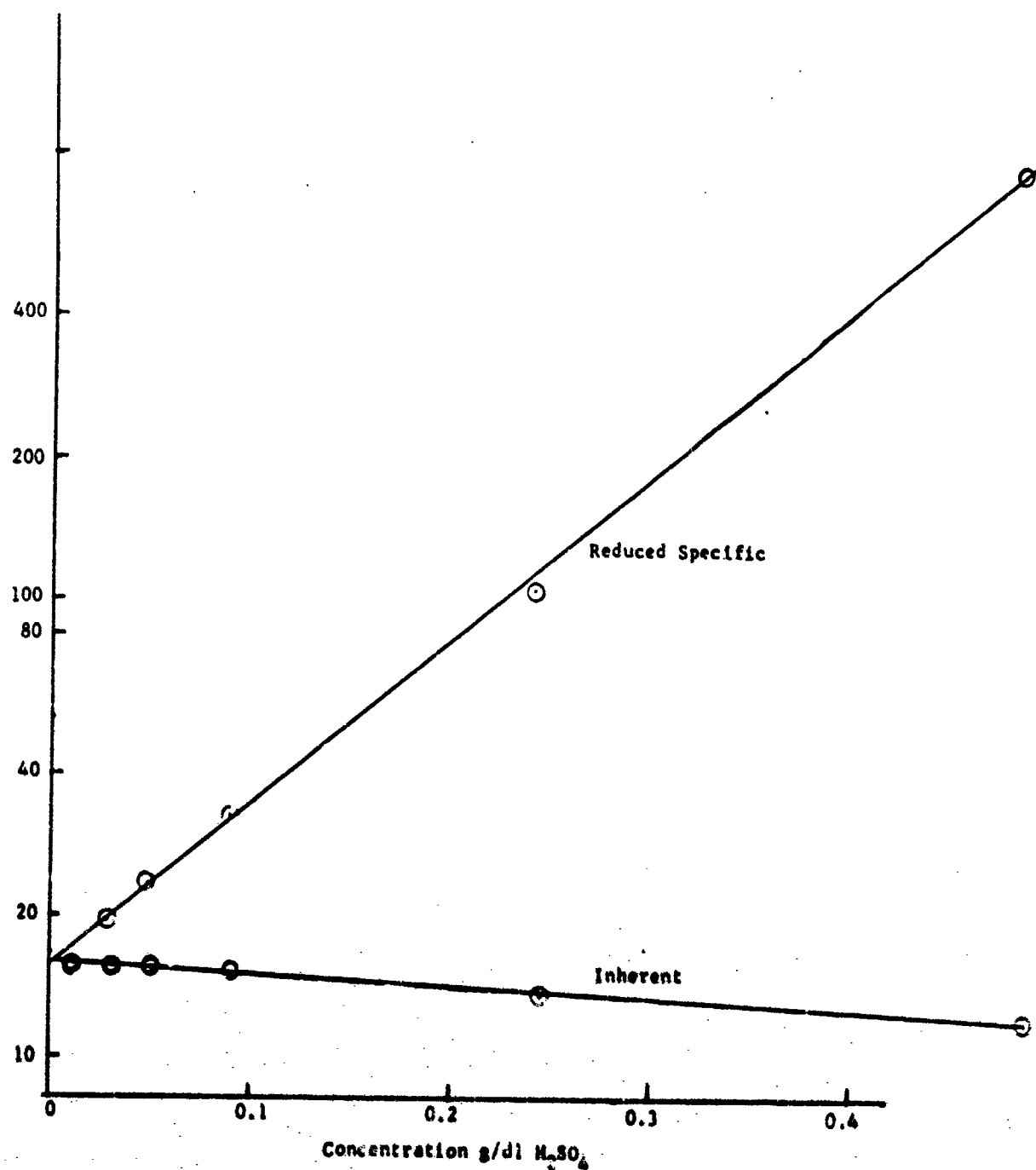


Figure 2. Intrinsic Viscosity of Polymer 2219-46 (AP-R-56)

TABLE V

SOLUBILITY DETERMINATION FOR PURIFIED AF-R-56 ( $\eta_{inh}$ -7.8)\*

<u>Solvent System</u>	<u>Percentage Polymer Solids</u>	<u>Room Temperature</u>	<u>Solubility</u> <u>14 Days Reflux</u>
96% Sulfuric Acid $H_2SO_4$	3%	Soluble	--
96% $H_2SO_4$	4%	Slowly soluble	--
96% $H_2SO_4$	5%	Incomplete solubility	--
85% Phosphoric Acid ( $H_3PO_4$ )	2.5%	Appears to be slowly soluble	--
98% Formic Acid ( $HCO_2H$ )	0.5%	Slowly soluble**	Slowly partially re-precipitates
98% $HCO_2H$	1%	Slowly soluble**	--
98% $HCO_2H$	2%	Slowly soluble**	--
Methanesulfonic Acid ( $CH_3SO_3H$ )	0.5%	Slightly soluble	Slightly soluble
$CH_3SO_3H$	1%	Slightly soluble	Slightly soluble
Dimethylacetamide (DMAC)	0.5%	Insoluble	Insoluble
Dimethylacetamide/ Lithium Chloride (6%) DMAC/LiCl	0.5%	Insoluble	Insoluble
Dimethylsulfoxide (DMSO)	0.5%	Insoluble	Solvent decomposition
Ethylene Glycol/ Potassium Hydroxide ( $KOH/CH_2OH)_2$ )	0.5%	Slowly soluble	--

\* 0.5%/ $H_2SO_4$ 

\*\* Solubilization accelerated at temperatures below 5°C.



Of the pure solvents tested, both sulfuric and phosphoric acids are the most powerful for AF-R-56 dissolution. The most useful system, with respect to wet spinning, however, is the m-cresol/formic acid sample. Each of these solvents systems is treated individually below.

(1) Sulfuric Acid. Prior to discovery of the m-cresol/formic acid solvent pair, 96% sulfuric acid had been found to be the most general solvent for the A-B PBI polymer, regardless of residual moisture content, state of subdivision or possible structural variations (imidazole vs. amino amide). Relative to the effect of the water content of the sulfuric acid, solubility is retained with  $H_2SO_4$  concentrations as low as 90%, although it appears to be only marginal at the 85% level. It may be possible to approach polymer solutions with  $H_2SO_4$  concentration lower than 90% by the controlled addition of water to a 90% sulfuric acid solution of the polymer, although this has not been tested. Solids content of these solutions does not appear to be dependent upon molecular weight. The handleable solution viscosities of the solutions obtained is, however, very much inherent viscosity dependent. The solids ceiling, is also much lower than desired. A polymer of  $\eta_{inh} = 3.0^*$  has a useable solids limit of about 5%, whereas with  $\eta_{inh} = 8.0^*$  polymer, the upper limit is about 2% solids.

(2) Phosphoric Acid. It has been shown in at least a single case, isolated AF-Y-56 polymer is capable of high solubility in 85%  $H_3PO_4$ . This polymer originated from polymerization of the monomer as the free base and was not given a refluxing concentrated ammonium hydroxide workup, and was found to be soluble to the extent of 10% solids at  $\eta_{inh} = 3.3^*$ . The remainder of the polymers prepared from the monomer as its hydrochloride salt have been found to be almost entirely insoluble in this solvent.

In contrast, however, all of the AF-Y-56 polymer preparations, regardless of origin, oxygen or water content, appear to be soluble in 100% phosphoric acid. The resulting  $H_3PO_4$  solution viscosities-solids concentrations-inherent viscosities relationships appear to be about the same as those with  $H_2SO_4$  and this polymer.

(3) Formic Acid/cresol. As alluded to above, the title solvent-pair system is most efficacious with respect to AF-Y-56 spinnability. The following studies summarize the behavior of the AF-Y-56 polymer in this solvent system.

(a) Clear solutions of the polymer in formic acid alone are not achieved at room temperature. Viscosity increases, however, are achieved as the polymer solids content is increased suggesting solubilization at least of low molecular weight polymer. At solids contents above ca. 12, undissolved polymer particles can be detected with the aid of crossed polarizers.

(b) The addition of a few percent of glycol, water or ethanol causes a gelation of a "solution" of the polymer in formic acid. The formic acid solutions also gel irreversibly upon heating.

\*  $0.5\% / H_2SO_4$

(c) The addition of m-cresol to the formic acid polymer "solution" at both 10 and 20 weight percent levels causes almost immediate clarification (below 1.5 solids content at RT), as verified by polarizing filters.

(d) All attempts to increase the solids content above 2.0% with high inherent viscosity ( $\sim 8.0$ )\* as well as with lower viscosity ( $\sim 3.0$ ), polymer at room temperature suggested that the 80/20 formic/cresol system was solids limited at this figure of 1.5%. At this concentration, the solutions become cloudy. Undissolved polymer has been detected in some, but not all, of these cloudy solutions under crossed polarizers. It was discovered that if the stirred solutions were placed in an ice bath, the cloudiness could be reduced or removed in most cases. This phenomenon was found to be reversible. Curiously, however, once the cloudiness has formed, it has not been possible to obtain a clear solution again by lowering the solids content by addition of fresh solvent mixture.

(e) Dissolution of AF-R-56 with a cold 80/20 formic/cresol mixture has always given a clear solution regardless of high or low inherent viscosity, up to 1.5% solids. Solubilization is more rapid at 0°C than at room temperature. These cold solutions exhibit pearlescent shear persistence.

(f) With regard to the composition of the solvent-pair itself, it has been further demonstrated that the initially chosen 80:20 ratio of formic acid:m-cresol is most satisfactory for the AF-R-56 system of high molecular weight. Thus, in a study designed to reduce the m-cresol concentration in the solvent pair, standard solutions were prepared, using polymer of  $\eta_{inh} = 16.6$  (0.005% in  $H_2SO_4$ ) (Code: N.B. 2217-39-A6), pulverized in a Wiley mill to pass a 40-mesh screen. With constant stirring at 0°C, solutions of 1% solids were attempted using 90:10, 85:15 and the standard 80:20 formic acid:m-cresol pairs. Only in the last case was total dissolution achieved. In the other two cases, more undissolved (gel-like) polymer remained with less m-cresol in the mixture. Visual observations were confirmed by a modified TGA study of the filtered solution samples.

In a second such study it was possible to dissolve low molecular weight A-B PBI polymer (N.B. Code 2217-18-B-7,  $\eta_{inh} = 3.1$ \*) in both the 85:15- and 90:10 formic acid:m-cresol pair at the 3.4%- and also at the 4.8%-solids levels. Both solutions displayed very high viscosity. Because of the low inherent viscosity of the polymer deployed for this pilot study, no spinning attempts were contemplated.

In a third study solvent pairs with increasing m-cresol content, above the standard 20%, were investigated for optimization of solubilization of high-inherent A-B PBI polymer thus 1% solids solutions of  $\eta_{inh} = 11.7$ \*\* (N.B. 2225-3-A10) were attempted at 0°C with standardized slow stirring, with the following solvent pairs:

\* 0.5%/ $H_2SO_4$

\*\* 0.005%/ $H_2SO_4$

N.B. Code	Solvent Pair Composition Formic Acid/m-Cresol (w/w)	Observation
2224-3-A4	70/30	Clear solution, no gellation
-3-A3	60/40	Clear solution, no gellation
-3-A2	50/50	Partial dissolution, much microgel
-3-A1	20/80	Polymer swollen, but no dissolution

It is already evident from this limited study that considerably higher m-cresol contents can probably be employed in these solutions. Since this component is the more difficult one to remove after spinning, no obvious advantage is to be gained. Consequently, the bulk of the subsequent higher solution concentration studies with high-inherent AF-R-56 were confined to the standard 80/20 formic acid/m-cresol composition.

g) The anisotropic  $\rightleftharpoons$  isotropic transition for solutions of the AF-R-56 in formic acid/m-cresol (80/20) occurs between 0°C and 25°C. It is further estimated that this transition most probably occurs between 5°C and 15°C, based on observable solution phenomena, such as solution viscosity changes, and birefringence differences to cross-polarized light.

The dissolution is best achieved by slow steady stirring, with either incremental or "all-at-once" addition of finely-powdered AF-Y-56 polymer, at or as close to 0° as possible, preferably using a shear stirrer. For these studies, a Hastelloy-C shear stirrer with offset vane spacings is preferred. This stirrer, which provides excellent agitation and mixing is pictured in Figure 3.

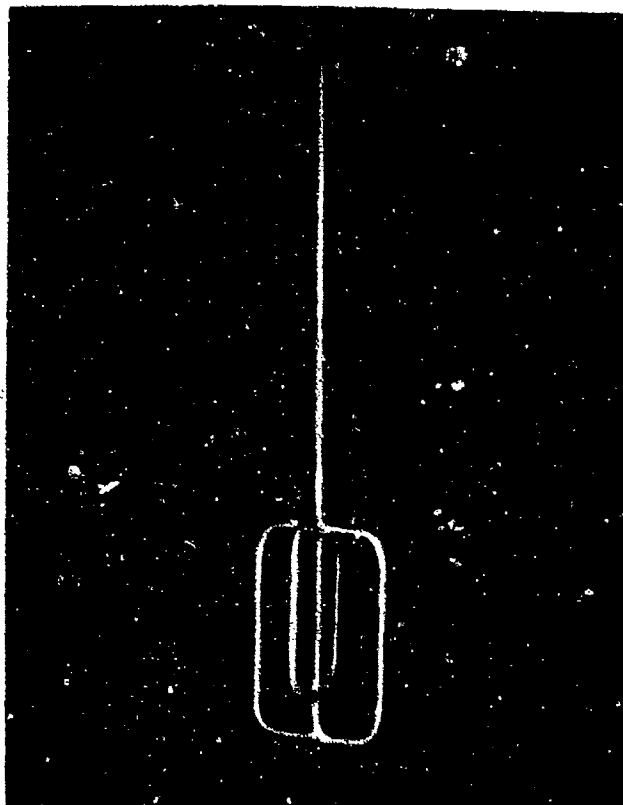


Figure 3. Hastelloy-C Shear Stirrer for High-Viscosity AF-Y-56 Solutions

(h) As will be discussed below, in the Wet Spinning Studies Section, a very high viscosity anisotropic (i.e., pearlescent) solution of high-inherent ( $\eta_{inh} = 10.11$ )\* AF-Y-56 polymer in 80/20 formic acid/m-cresol has been prepared by the above techniques at 2.0% solids. This solution, with its high viscosity (estimated to be ca. 2000-3000 poise) presented some difficulty in de-gassing, but spun successfully to high-quality yarn, as is discussed below.

(i) Since it was possible to spin this solution despite the high-viscosity, even higher solids content solutions have been prepared. Thus, solutions of  $\eta_{inh} = 10.1$  AF-Y-56 in 80/20 formic acid/m-cresol have been prepared albeit, with extremely high viscosities, at the 2.5% solids level. It was not possible, however, to extrude this high viscosity solution through a 3-mil screen, in an attempt to lower the solution viscosity by the imposition of high shear. Thus, spinning studies have been confined to the 1.0-2.0% solids regime.

\* 0.005%/H<sub>2</sub>SO<sub>4</sub>

Thus, it appears that the formic acid-cresol mixture provides an ordered solution at low temperature, and that the ordering is reduced when dissolution is effected at room temperature. The implications of this atypical solubility with regard to wet spinning are discussed below.

### 3. Wet Spinning Studies

The wet spinning of solutions of AF-R-56 can be divided into two parts:

- a) mineral acid dopes (sulfuric and phosphoric), carried out in the earlier phase of this program; and,
- b) formic acid/m-cresol dopes, with varying solids content, spun initially into ethyl ether coagulant, and, later, into the more satisfactory ethyl acetate coagulant.

These two spinning solution types are discussed separately below.

#### a. Spinning Equipment

In anticipation of an eventual scale-up to gallon quantities of spinning solution, and larger, installation and final assembly of our complete, heavy-duty wet spinning unit was accomplished early on the program. This unit has been engineered to deliver spinning solutions with solution viscosities as high as several thousand poise, in quantities from 500-ml to 16-gallon, throughout a wide range of pump speeds and spinning speeds.

A stainless steel Continental (Moyno-type) pump and 1/2 HP Varidrive has been installed. A three gallon vessel with necessary circulation and degassing facilities was also constructed. This vessel has been used to supply the Continental metering pump for delivery to the spinneret.

A three-gallon Sparkler filter with attendant 1-HP stainless steel Viking circulating pump is also included in the spinning cell. This unit has been used as a combination filtering unit and supply hopper for supplying spinning solution to the above-mentioned metering vessel. The reservoir for this filter unit is a similar vessel from which the filter has been removed.

A Leeson #959 constant-tension take-up machine, along with a Leeson #950 take-up machine, were also included. The Leeson #950 take-up unit was slightly revamped for our purposes. In addition a Leeson #959 constant tension take-up machine has been used for repackaging yarn. A small Leeson #50 machine, with a new 1-HP motor and more efficient cam and pulley, to operate at constant slow speed was used for the

direct windup. This last unit was also used with the simple monofilament spinning which is discussed later in the report.

In addition to the above spinning equipment, a large spinning bath (12-ft length x 1-ft width; 80-gallon capacity) has been constructed and installed. With a 20-kw preheater unit and in-bath heating coils (13 kw total), the bath is capable of maintaining 90°-95°C aqueous operation at a replenishment rate of 1-gallon/minute. It has also been fitted with the detachable split bath components for complex coagulation.

The entire spinning cell is diagrammed in Figure 4.

For our smaller spinning scale, however, the bulk of the spinning studies have been batch runs, using the same bath and windup assembly as above, but substituting a Bodine 1/4-HP motor-driven displacement drive shaft for the metering pump from the larger unit. The spinning solution feed supply was a Delrin cylinder (3 in. O.D. x 2 in. I.D.) fitted with a piston of the same material. The spinneret pack mounted at the outlet of the cylinder contained the spinneret (typically 3-mil holes) backed by polypropylene felt (porosity-20, uncalendered) and a distribution plate. This unit provided uniform delivery, essentially independent of solution viscosity at the 1 to 2% solids level, with a maximum capacity of 250-ml. Two of these piston drive feed units have been constructed to allow facile interchange for higher yarn output.

#### b. Wet Spinning Studies from Formic Acid/m-Cresol Dopes

As indicated above, the most useful solvent system for the AF-Y-56 polymer for multifilament spinning has been formic acid/m-cresol (80/20) at ca. 0°C. Initial studies with this system utilized diethyl ether as a coagulating medium. As will be shown below, ethyl acetate was found to be equally satisfactory for coalescence of the AF-Y-56 system, and, at least in several cases, superior as-spun yarn was produced in this latter medium, especially at the dope solids level of 1.4 or higher.

Tables VI and VII list representative earlier spinning studies at the 1.0% solids level into ethyl ether. In both these tables, a significant effect of spin stretch on as-spun tensile properties at this low solids level has been observed. Thus, as seen in Table VI, the spin-stretch-factor appears to be a critical determinant of residual plasticization of the fiber, as reflected in the extensibility. Virgin as-spun yarn after 150°C oven pre-treatment (30 min) routinely exhibits a tenacity range of 4-7 grams per denier, with an elongation range of 20-50%, and initial modulus of 60-120 grams per denier.

Within the useful spinning limits, with polymer inherent viscosity  $\geq 10$  ( $H_2SO_4$ )\*, higher tenacities and initial moduli are obtained with higher spin stretch factors to a limit, at the expense of the elongation attributed to plasticization. Examples of this effect have been abstracted into Table VIII.

\* 0.005%/H<sub>2</sub>SO<sub>4</sub>

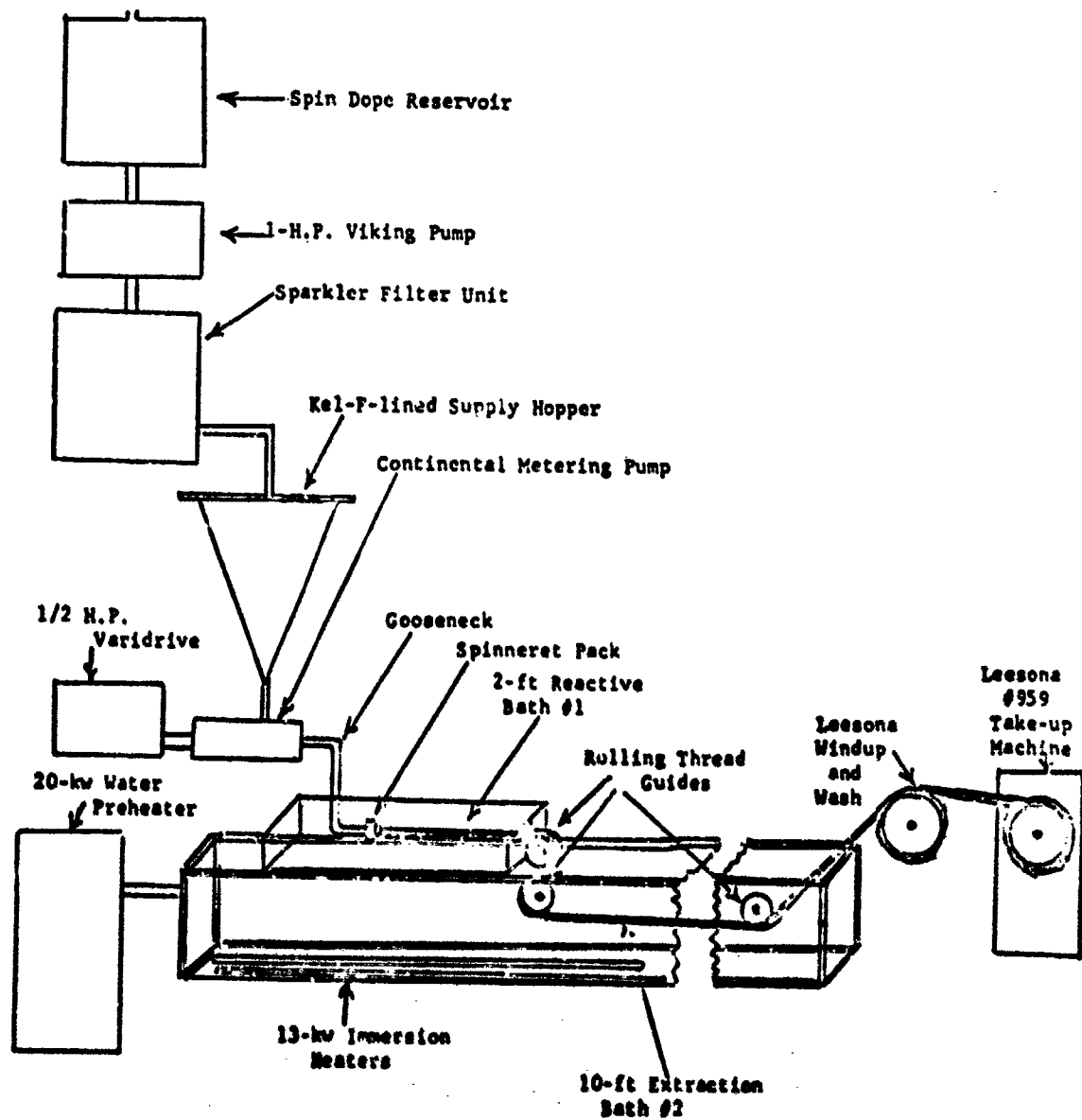


Figure 4. Schematic Representation of Split-Bath Wet-Spinning Cell

TABLE VI

AF-Y-56 WET SPINNING SUMMARY<sup>(1)</sup> -- SPIN STRETCH EFFECTS

SPINNING PARTICULARS				FIBER PROPERTIES									
Polymer M.B. 2217-	Dope K.B. 2224-	Yarn M.B. 2224-	Filaments	Pump Rate (g/min)	Spin Stretch ( $V_2/V_1$ )	Denier (Calc'd)	Denier (Dry) (5)	Tenacity (g/den)	Elonga- tion (%)	Modulus, Initial (g/den)	Tensile Factor TEL/2 (6)	Denier (Condit.) (7)	% Moisture Regain
46-A10 T <sub>inh</sub> = 14.4; 15.2 (0.005%)	1-11/12	21-A1 (2)	778 x 3 ml	1.4	2.3	168	165	4.2	63	79	33.4	190	15
		-A2	↓	2.0	1.1	239	238	3.1	66	76	25.1	282	19
		-A3	↓	2.8	2.1	180	141	4.7	39	91	29.4	159	13
			↓	2.8	4.0	97	86	4.8	15	108	18.4	95	11
50-A10 T <sub>inh</sub> = 35.8 (0.005%)	1-A9/AS	17-A1 (3)	684 x 8 ml	3.8	16.7	14	429	3.0	42	50	19.8	579	35
		-A2	↓	↓	26.1	92	125	3.6	24	73	17.3	160	29
		-A3	↓	↓	35.9	67	89	3.4	19	83	14.6	116	31
		-A4	↓	↓	51.9	46	45	3.0	14	83	11.1	60	34
		-B	↓	↓	53.1	45	68	2.4	13	72	8.6	88	29
		-C	↓	↓	64.5	37	57	2.4	11	62	7.9	73	29
		-D	↓	↓	↓	↓	100	2.1	16	52	8.4	132	31
		-E	368 x 8 ml	5.5	18.8	37	68	2.4	80	73	19.2	↓	↓
	1-A6	13-1A (2)	195 x 7.5 ml	3.8	3.8	160	143	2.4	34	54	13.8	160	13
		-2A	↓	↓	4.6	131	132	2.4	33	61	14.0	149	13
		-3A	↓	↓	6.0	99	102	2.8	27	71	14.3	116	14
		-4A	↓	↓	7.3	83	92	2.6	27	69	13.2	104	14
		-5A (2)	↓	↓	9.1	66	69	2.4	19	71	10.5	82	18
		14-4B	↓	2.2	16.7	61	39	2.1	37	43	12.7	42	9

(1) All spinning solutions were 80/20 formic/cresol with 1.0% solids polymer spun into ethyl ether

(2) 5-foot bath length

(3) 20-foot bath length

(4)  $V_2/V_1$  = Windup rate (mm/min)/pump rate (mm/min)

(5) Dried 1 hr @ 150°F

(6) Reference No. 4

(7) Conditioned 24 hr @ ambient temperature @ 70% RH



TABLE VII  
AF-Y-56 WET SPINNING SUMMARY<sup>(1)</sup> -- SPIN STRETCH AND BATH TEMPERATURE EFFECTS

Polymer M.B. 2217-	Dope M.B. 2224-	Yarn M.B. 2224-	SPINNING PARTICULARS				FIBER PROPERTIES					Bath Temperature (°C)
			Filaments	Pump Rate (g/min)	Spin Stretch ( $V_2/V_1$ )	Denier (Calc'd)	Denier (Dry) (3)	Tenacity (g/den)	Elongation (%)	Modulus, Initial (g/den)	Tensile Factor TEL/2	
46-A10 $\eta_{inh} = 15.2$ 0.005% $H_2SO_4$	1-A13	25-B1	596 x 3 md1	1.2	3.1	78.7	73.6	4.8	26	95	24.4	14
		25-B2	596	1.2	5.6	43.5	42.7	6.1	18	112	26.0	14
		25-B3	596	1.2	5.6	43.5	40.2	5.8	17	121	24.3	6
		25-B4	596	1.2	5.6	43.5	36.2	6.1	10	139	19.3	-5
		25-B5	596	1.2	5.6	43.5	40.4	5.9	8	126	17.4	-12
46-A10 $\eta_{inh} = 15.2$ 0.005% $H_2SO_4$	1-A10	33-A1-2	780 x 3 md1	1.9	2.8	139.3	104.7	6.9	21	97	32.1	--
		33-A1-3	780	1.9	3.2	119.0	85.8	6.4	13	110	22.7	5.5
		33-A1-4	780	1.9	3.8	100.0	79.8	6.6	11	119	22.0	2.5
		33-A2-1	780	1.9	2.9	131.7	99.3	6.2	16	77	24.3	0
		33-A2-2	780	1.9	2.3	166.6	119.9	5.3	38	71	32.6	0
46-A10 $\eta_{inh} = 15.2$ 0.005% $H_2SO_4$	1-A10	33-A3-1	990	1.9	2.9	166.6	130.5	6.4	21	88	29.3	-2
		33-A3-2	990	1.9	2.4	199.6	162.0	6.1	30	80	33.2	-2
		34-A1-1	1220 x 3 md1	3.2	1.4	421.6	297.0	5.9	60	74	45.3	11
		34-A1-2	1220	3.2	0.8	765.6	566.1	4.2	59	59	32.6	7
		34-A2-1	1220	3.2	0.8	765.6	574.2	4.2	59	59	32.6	6
46-A10 $\eta_{inh} = 15.2$ 0.005% $H_2SO_4$	1-A5	34-A2-2	1220	3.2	1.1	559.5	509.5	3.8	45	62	25.1	5
		35-A1	596 x 3 md1	3.2	0.5	554.3	349.2	3.9	78	57	34.8	10
		35-A2	780	3.2	0.7	561.3	362.7	5.2	53	67	37.6	8
		35-A3	990	3.3	0.8	578.8	413.1	4.5	56	60	33.6	3
		35-B1	1100	3.4	1.0	530.8	437.4	5.5	38	74	34.1	3
46-A10 $\eta_{inh} = 15.2$ 0.005% $H_2SO_4$	1-A5	35-B2	890	3.2	0.9	495.2	417.6	5.0	48	68	34.5	3
		35-B3	990	3.4	0.9	526.1	421.2	5.1	45	69	34.0	2
		35-C1	780	3.4	0.9	447.3	454.5	4.6	54	68	33.6	1

(1) All spinning solutions were 80/20 formic/cresol with 1.0% solids polymer spun into ethyl ether  
(2)  $V_2/V_1$  = Windup rate (mm/min)/pump rate (mm/min)  
(3) Dried 1 hr @ 150°F

TABLE VIII

## EFFECT OF SPIN STRETCH ON AS-SPUN AF-Y-56 PROPERTIES

<u>Fiber Code</u>	<u>Spin Stretch* Factor <math>V_2/V_1</math></u>	<u>Denier</u>	<u>Tenacity</u>	<u>Elongation</u>	<u>Modulus Init.</u>
2224-25-B1	3.06	74	4.8	26.4	95
2224-25-B4	5.62	36	6.1	10.0	140
2224-25-A1	2.59	73	6.5	23.4	120
2224-25-A2	6.14	55	7.6	6.9	175
2224-33-A1-4	3.83	80	6.6	11.2	120
2224-33-A1-1	2.91	99	6.2	15.6	77

\* Spin stretch factor,  $V_2/V_1$  = windup speed/pump speed

Inspection of Table VII suggests that a relationship exists between the bath temperature employed to produce the yarn and the elongation of the resulting yarn. Higher bath temperatures appear to be associated with higher elongations in the yarn.

The maximum level of tenacity development in ether coagulant was 6.9 gpd (Table VII, Yarn N.B. 2224-33-A1-2). The tensile properties of this yarn ( $T/E/M/TEL/2 = 6.9/21/97/32$ ) compare well with optimized as-spun properties obtained with higher solids dopes, as discussed below.

Table IX summarizes a series of spins conducted with dopes in the 1.0-1.5% solids range, with little distinct property variation for the increased solids, compared to the 1%-solids dopes. That these fibers retain plasticization after a 105°C/60 min drying cycle is indicated from the high break elongation levels. When these yarns were dried at 140°C a marked improvement in tenacity was realized, and the elongation levels became stabilized at lower level. The tensile factors ( $TEL/2$ ) for these yarns were not materially affected by the different drying cycles, as shown in Table X.

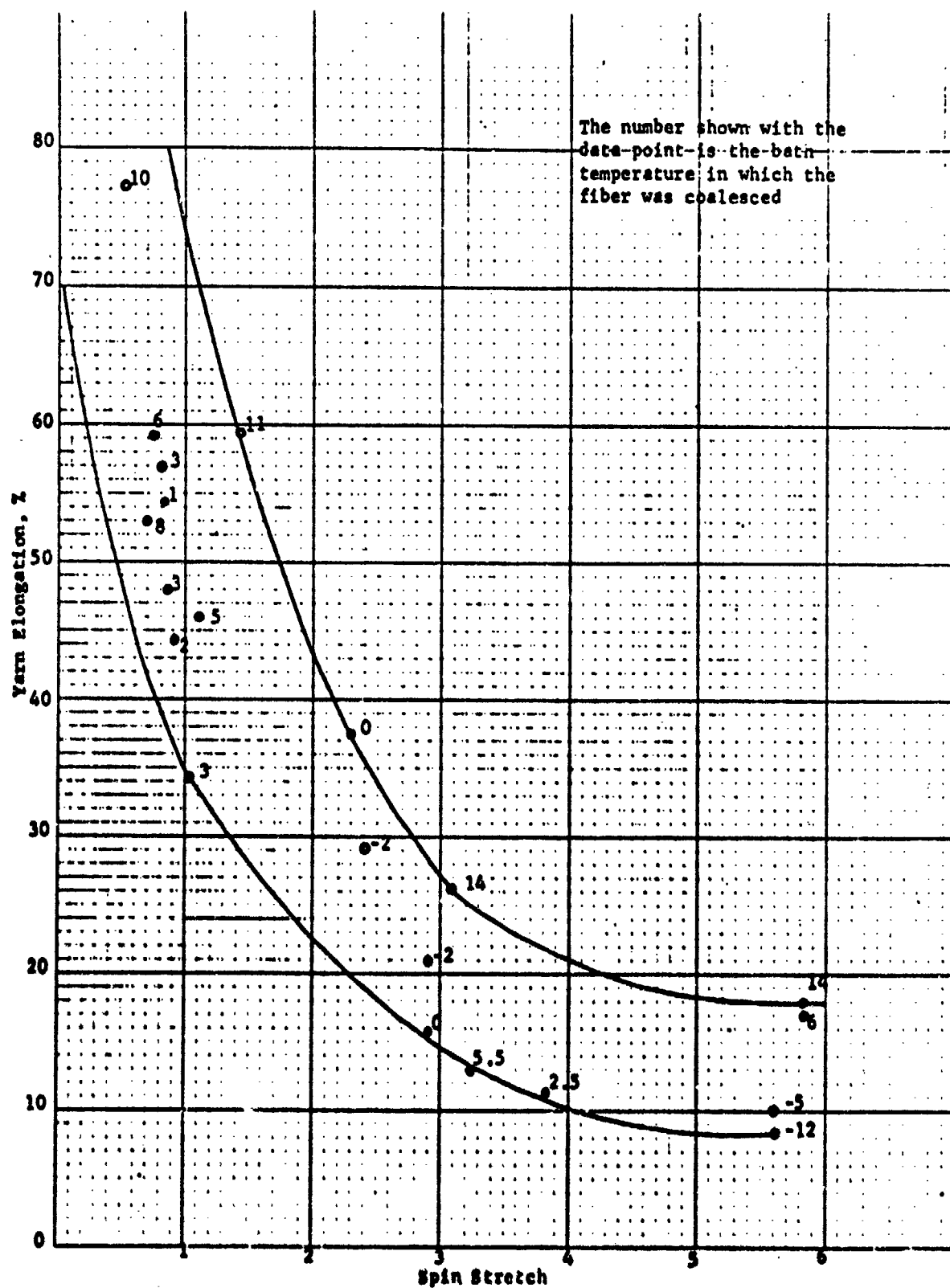


Figure 5. The Effect of Spin Stretch on Yarn Elongation

TABLE IX

AF-Y-56 WET SPINNING SUMMARY<sup>(1)</sup> -- EFFECT OF DOPE SOLIDS

Polymer S.B. 2217-	Dope M.B. 2224-	Yarn M.B. 2224-	SPINNING PARTICULARS			FIBER PROPERTIES				Modulus, Initial (g/den)	Tensile Factor TEI/2	Spinning Bath Temperature (°C)
			Filaments	Pump Rate (g/min)	Stretch (V <sub>2</sub> /V <sub>1</sub> )	Denier (Calc'd)	Denier (Dry)	Tenacity (g/den)	Elongation (%)			
39-A6 R <sub>1</sub> = 16.6 0.005% H <sub>2</sub> SO <sub>4</sub>	1-A14	35-D1	779 x 3	3.2	0.77	495		Not suitable for test		39	30.4	13
	1.0Z	35-D2	↓	3.4	0.69	559	412	3.3	84			7
		35-D3		3.3	0.49	789		Not suitable for test				7
50-A10 R <sub>1</sub> = 15.8 0.005% H <sub>2</sub> SO <sub>4</sub>	1-A15	36-A1	779 x 3	3.2	0.69	648	389	3.8	59	59	29.5	11
	1.2Z	36-A2	596 x 3	3.0	0.37	920		Not suitable for test				0
		36-A3	779 x 3	3.3	0.49	920	571	2.2	150	34	27.2	0
		36-B1	↓	3.1	0.80	559	378	2.7	88	44	24.9	1
		36-B2		2.4	0.56	802						0
50-A10 R <sub>1</sub> = 15.8 0.005% H <sub>2</sub> SO <sub>4</sub>		36-B3	↓	3.1	0.43	1046	637	1.8	142	31	21.8	1
	2-B1	51-A1	596 x 3	3.3	0.44	723		Not suitable for test				15
	1.1Z	51-A2	↓	3.1	0.65	490	411	2.9	99	37	29.0	12
		51-B1		3.1	0.79	401	358	3.4	86	41	31.2	7
		51-B2		3.2	1.00	364	319	3.3	73	41	28.5	7
46-A10 R <sub>1</sub> = 15.2 0.005% H <sub>2</sub> SO <sub>4</sub>	2-B2	2232-1-A1	↓	2.7	2.8	95	81	4.1	34	60	23.7	15
	1.0Z	-1-A2		2.9	3.0	85	72	3.8	35	58	22.3	7
		-1-A3		2.5	3.6	74	66	3.7	27	54	18.9	4
	3-B3	-2-A1	571 x 3	2.7	2.37	138	137	4.3	33	59	24.5	13
	1.2Z	-2-A2	530 x 3	3.1	1.56	204	193	3.6	46	46	24.5	5
50-A10 R <sub>1</sub> = 15.8 0.005% H <sub>2</sub> SO <sub>4</sub>		-2-A3	580 x 3	3.1	2.65	125	137	3.5	31	52	19.3	2
		-2-A4	580 x 3	3.1	1.36	245	272	2.9	64	36	22.8	0
	3-B2	-2-B1	580 x 3	3.0	1.34	231	238	3.4	55	40	24.9	9
	1.1Z	-2-B2	554 x 3	3.1	1.65	174	213	3.0	46	39	20.2	2
		-2-B3	554 x 3	3.3	2.01	147	151	3.8	24	58	18.5	4
4-B4 1.3Z		-3-C1	580 x 3	2.8	2.05	174	211	4.2	31	55	23.2	12
		-3-C2	580 x 3	2.7	2.33	154	184	3.9	20	59	17.7	8
		-3-C3	540 x 3	3.2	2.10	157	172	3.7	21	58	17.0	4
	4-B6	-3-D1	500 x 3	3.1	2.27	162	152	3.7	29	60	19.9	6
	1.5Z	-3-D2	530 x 3	3.3	1.77	221	207	3.3	28	51	17.3	4
4-B5 1.4Z		-3-D3	530 x 3	3.0	1.26	311	340	2.9	47	41	20.2	5
		-4-E1	530 x 3	3.1	1.20	290	211	3.9	40	52	24.7	9
		-4-E2	530 x 3	3.1	1.66	210	200	4.1	33	58	23.5	6
		-4-E3	554 x 3	3.2	1.94	188	179	4.1	29	63	22.2	2
		-4-E4	554 x 3	3.2	2.11	172	171	4.1	25	62	20.6	2

(1) All spinning solutions were 80/20 formic/acetol spun into ethyl ether  
 (2)  $V_2/V_1$  = Windup rate (mm/min)/pump rate (mm/min)

TABLE X  
EFFECT OF 150°C-DRYING ON TENSILE PROPERTIES OF  
AS-SPUN AF-Y-56 (ETHER COAGULANT)

<u>Fiber No.</u>	<u>Drying Conditions</u>	<u>Denier</u>	<u>% Decrease</u>	<u>T/E/Mi</u>	<u>% T Increase</u>	<u>Failing Load, g</u>	<u>% Increase</u>	<u>TE<sup>1/2</sup></u>
-2-B1	105°C/60 min	238		3.4/55/40		796		24.9
	140°C/45 min	209	11	4.9/27/100	44	1025	29	25.3
-2-B2	105°C/60 min	213		3.0/46/39		632		20.2
	140°C/45 min	199	7	5.2/30/118	73	1030	63	20.5
-4-E3	105°C/60 min	179		4.1/29/63		742		22.2
	140°C/45 min	172	10	6.1/14/128	49	1054	42	22.7
-4-E4	105°C/60 min	171		4.1/25/62		702		20.6
	140°C/48 hr	158	9	6.0/12/98	46	952	36	21.0

When ethyl acetate was substituted for ethyl ether at the increased solids level (1.4%), however, superior AF-Y-56 was obtained. Thus, from the data shown in Table XI, it can be seen that the same AF-Y-56 dope, when spun into ethyl acetate with comparable spinning conditions to those used for standard ether coagulation, produced lustrous as-spun fiber, with tenacity levels as high as those obtained in ether. The most remarkable facet of this initial comparative study lies in the fact that the ethyl acetate-spun yarn retained ca. three times the elongation level, regardless of spin stretch level. This difference obviously provided for a significantly higher tensile factor level, and indicated that ethyl acetate is a better coagulant medium for the AF-Y-56 system than is ethyl ether.

With the eventual preparation of formic acid/m-cresol dopes of AF-Y-56 in the 1.7-2.0%-solids range, the effect of solution viscosity upon fiber spinnability and as-spun tensile property development level became apparent. As can be seen from the data in Table XII, maximum tensile properties ( $T/E/Mi/Den = 7.4 \text{ gpd}/29.6\%/97 \text{ gpd}/332$ ), with an impressive tensile factor:  $TE^{1/2} = 40.3$ , were obtained with the greater fluidity at the 1.7% solids level. The polymer (N.B. 2225-7-A8) had an inherent viscosity of 17.1.\* From this same series, with a different polymer batch (N.B. 2225-7-A8) of lower viscosity ( $\eta_{inh} = 10.1$ )\* at the 2.0% solids level, a maximum tensile factor of 33.3 was obtained, at a more modest tensile property level ( $T/E/Mi = 5.0 \text{ gpd}/44.3\%/71 \text{ gpd}$ ).

This difference in spinning performance and fiber property development reflects several effects, primarily the difference in inherent viscosity as well as in solution viscosity. When the same high viscosity polymer ( $\eta_{inh} = 17.1$ )\* was used at the 2.0%- and also at the 1.7%-solids level, with the larger spinning unit, a similar trend in as-spun properties was realized, as shown in Table XII.

Thus, the 1.7% solids dope produced an enhanced level of as-spun tensiles, with  $T/E/Mi = 6.6 \text{ gpd}/20\%/86 \text{ gpd}$ , for a  $TE^{1/2} = 30$ , obtained from this dope. A maximum tenacity level of 5.0 gpd was obtained from the more viscous 2.0% solids dope. These spins cited in Table XII all suggest that spinning conditions can be improved further to provide for higher as-spun tensile factor levels. (NOTE: All the bobbins obtained were soaked for an additional 30 minutes in ether, then dried for 1 hr at 150°C prior to testing.)

#### c. Effect of Moderate Heat-Treatment on As-Spun AF-Y-56

In order to more accurately define as-spun AF-Y-56, the effect of even higher drying temperatures on tensile properties, and on tensile factor development was investigated. This study was carried out on yarn produced from 1.9-2.0% solids dopes spun into ethyl acetate. A general increase in tenacity was realized with 300°C drying, in skein form, relative to 150°C drying, with a variable effect on tensile factor. These effects are summarized in Table XIII.

\* 0.005%  $H_2SO_4$

TABLE XI

COMPARISON OF AF-Y-56 AS-SPUN YARN PROPERTIES  
FROM ETHYL ACETATE VS. DIETHYL ETHER COAGULANT \*

Coagulant	Yarn M.B. 2232-	Filaments	SPINNING PARTICULARS			FIBER PROPERTIES					
			Bath Temp., °C	Pump Rate (g/min)	Spin Stretch ( $V_2/V_1$ )	Denier (Calc'd)	Denier (Dry) **	Tenacity (g/den)	Elonga- tion (%)	Modulus, Initial (g/den)	Tensile Factor TEL/2
Ethyl Acetate	-7-A1	554	12	2.82	2.02	180	198	5.9	30	73	35.5
	-7-A2	563	15	2.82	1.38	267	196	6.0	34	73	35.0
	-7-A3	563	15	2.82	2.76	134	151	6.4	29	87	34.5
Diethyl Ether	-4-E4	554	?	3.2	2.11	172	158	6.0	12	98	21.0

\* All spun from Dope No. 2224-4-B5, @ 1.42 solids.

\*\* All fibers dried 45-60 min @ 140°-150°C prior to testing

TABLE XII

AF-Y-56 WET SPINNING SUMMARY -- ETHYL ACETATE COAGULATION\* -- DOPE SOLIDS EFFECT

Polymer	Expt	Yarn N.B. 212-	Filaments	Pump Rate	Spin Stretch	Densit (Calc'd)	Densit (Dry)	Tenacity	Elonga- tion (%)	M <sub>i</sub>	TE <sup>1/2</sup>	% Dope Solids
2225-7-AS Yarn - 10.1	2224-4- B10	10-E1	563 ± 3	2.75	0.918	603.1	520.2	4.3	40.0	61	27.4	2
		10-E2	↓	2.75	0.918	603.1	533.7	4.4	43.5	61	29.0	↓
		10-E3	↓	2.75	0.918	603.1	539.5	4.5	42.0	61	29.3	↓
2225-7-AS	2224-4- B11	10-F1	368 ± 3	2.34	0.624	580.5	413.1	5.0	44.3	71	33.3	2
		10-F2	↓	2.30	1.427	253.8	201.6	5.3	27.4	79	27.8	↓
		10-F3	↓	2.06	0.974	371.9	332.1	4.7	40.4	68	30.1	↓
		10-F4	↓	2.06	0.885	409.3	347.4	4.1	36.8	64	24.8	↓
2225-11-AS Yarn - 17.1	2224-4- B13	11-B1	596 ± 3	2.20	1.521	289.3	230.8	6.3	28.4	90	33.7	1.5
		11-B2	↓	4.35	0.769	572.2	232.2	6.7	31.1	88	37.1	1.5
	2224-4- B14	11-C1	596 ± 3	2.50	0.983	328.9	332.1	7.4	29.6	97	40.3	1.7
		11-C2	↓	2.50	2.130	151.8	155.2	6.3	21.4	100	29.2	1.7
	2224-4- B15	12-B1	↓	5.70	1.39	422.4	439.0	5.0	17.0	83	20.0	2.0
		12-F1	438	5.20	0.76	570.2	480.6	4.3	28.0	66	23.0	2.0
	2224-4- B16	12-G1	596	4.65	1.78	275.5	282.6	6.6	20.0	96	29.0	1.7
		12-H1	↓	5.00	1.46	335.8	323.1	6.7	26.4	88	34.3	1.7
	2224-4- B16	12-I1	↓	6.30	1.22	480.5	361.8	5.0	14.3	119	19.0	2.0

\* All spun into ethyl acetate @ 20-20°C; all yarn samples dried 1 hr @ 150°C.



TABLE XIII

EFFECT OF DRYING TEMPERATURE ON AS-SPUN AF-Y-56 PROPERTIES\*

Dope	M.B. 2232-	Drying Temp	Dens	Tenacity	Elonga- tion (%)	M <sub>1</sub>	TE <sup>1/2</sup>
2232-24-A1 1.9% solids	2232-13-A1	300°C	306	5.7	18.8	129	24.5
2232-24-A2 2% solids	2232-24-A2	150°C	234	3.9	41.8	65	25.2
	2232-24-A2B	300°C	225	6.0	20.1	121	26.9
2224-4-B16 2% solids	2232-13-A3	150°C	360	4.6	17.6	111	19.2
	2232-13-A3B	300°C	321	5.9	21.5	127	27.3
2224-4-B8 2% solids	2232-10-B4	150°C	413	5.0	44.3	71	33.3
	2232-10-F1B	300°C	400	4.7	45.8	46	31.6
	2232-10-F2	150°C	202	5.3	27.4	79	27.8
	2232-10-F2B	300°C	203	5.5	26.5	80	28.1
2224-4-B8 2% solids	2232-8-B3	150°C	350	5.6	41.0	70	35.9
	2232-8-B3A	250°C	295	6.4	32.1	85	36.3
	2232-8-B3B	300°C	267	7.0	32.0	94	39.5
	2232-8-B3C	400°C**	265	7.1	23.0	104	33.8

\* Fibers dried in sheet form in circulating air except as indicated

\*\* Heat treatment carried out under nitrogen

In one study cited in Table XIII (N.B. 2232-8-B3 yarn), 150°C-, 250°C-, and 300°C-cycles in air, as well as a 400°C-cycle in nitrogen, were compared. A remarkably high tensile factor level, namely:  $TE^{1/2} = 39.5$ , was obtained ( $T/E/Mi = 7.0/31.7/93.5$ ) from the 300°C/1 hr drying cycle. At higher drying temperatures, a decrease in tensile factor was observed, corresponding to an enhancement in initial modulus at the expense of break elongation.

It, therefore, appears reasonable for textile fiber applications for AF-Y-56 to utilize a 300°C drying cycle to define as-spun yarn. For heat treating purposes, however, as discussed in the following section, no appreciable differences in final tensile properties have been realized as a result of the more stringent drying of the input as-spun yarn.

#### d. High-Temperature Heat Treatment of AF-Y-56

In order to convert the as-spun AF-Y-56 fiber to a high-tenacity, high-modulus oriented fiber for high-temperature evaluation, advantage has been taken of the response of this fiber to on-the-run heat treatment. A tube furnace fitted with a nitrogen blanket at both input and outlet has been used for the studies described below. The addition of a vari-load, in-line tensiometer, capable of registering running tension ranges from 5 to 2000 grams, has provided for both an increase in running velocity (necessary with higher temperature treatment), and a method for additional quantification (hence, reproducibility) of heat-treatment conditions. In addition, high rpm drive motors have also been installed to provide a wider range of more reproducible furnace residence times, of from ca. two to eighteen seconds.

Using these equipment modifications, it has been possible to utilize oven temperatures as high as 1000°C\*, under which conditions a relaxation of the fiber has been observed. With ethyl acetate coalesced yarn, multiple passes at high speed have also been possible. Thus with two passes at 1000°C, it has been possible to prepare, in two cases, yarn with tenacities above 13 gpd, and initial moduli of 500 gpd. The strongest yarn to date, from such treatment displayed  $T/E/Mi/TE^{1/2} = 13.3 \text{ gpd}/2.2\%/501/19.7$ . Thus, this yarn property level represents a doubling of the as-spun tenacity with an almost five-fold increase in initial modulus. These effects are listed in Table XIV.

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\* NOTE: The temperatures recorded are by thermocouple, and represent the oven temperature. The actual yarn temperature has not yet been determined, and is probably much lower than the oven temperature, especially at high throughput speeds.

TABLE XIV

## HEAT TREATMENT SUMMARY OF AS-SPUN AF-Y-56 FROM ETHYL ACETATE COAGULATION

AS SPUN YARN										HEAT TREATED YARN					ΔMI, %
Hot Stretch Code	Parent Fiber	Dry Denier	Tenacity	Elonga- tion	Initial Modulus	1/2 TE	Max. Temp °C	Dry Denier	Tenacity	Elonga- tion	Initial Modulus	1/2 TE	ΔT, °C		
2232-34-B1	2232-12-C1	282.6	6.6	19.8	96	29.3	850	229.0	9.8	2.4	386	23.2	49	302	
2232-34-C1	2232-12-B1	323.1	6.7	26.4	88	34.3	800	236.7	7.1	1.3	450	9.7	6	411	
-34-C2							800	242.4	10.4	1.7	477	13.6	55	462	
-35-C3							900	270.0	10.0	3.0	370	17.2	49	320	
-35-C4A							400	331.3	6.0	17.4	103	25.0	-10	17	
-35-C4B							700	238.4	7.7	2.0	371	11.0	15	322	
-36-C5A							800	217.2	11.7	2.1	470	16.9	75	434	
-36-C5B							850	233.5	10.6	2.1	466	15.4	58	430	
-36-C6A							900	236.1	10.5	2.2	519	15.6	57	490	
-36-C6B							1000	236.5	10.6	2.0	547	15.0	58	522	
-36-C7A							800	256.7	9.8	1.8	486	13.2	46	452	
-36-B1	2232-12-B1	361.8	5.0	14.3	119	19.0	800	248.1	8.6	1.7	457	11.2	72	284	
2232-37-E1	2232-12-B1	323.1	6.7	26.4	88	34.3	1000	258.6	11.2	3.2	400	20.0	67	355	
-37-E2							1000x2	247.9	11.2	2.3	448	17.0	67	409	
-37-E3							600	226.3	8.5	1.6	501	10.8	27	469	
-37-E4							800	223.2	9.3	2.3	478	14.1	39	443	
-37-E5							1000	224.0	13.1	2.2	506	19.4	96	475	
-38-F1							1000x2	231.1	13.3	2.2	501	19.7	99	469	

\* ΔT = T<sub>HT</sub> - T<sub>AS</sub> / T<sub>AS</sub> ; ΔMI = MI<sub>HT</sub> - MI<sub>AS</sub> / MI<sub>AS</sub>

TABLE XIV (Continued)

AS SPUN YARN												HEAT TREATED YARN			
Hot Stretch Code	Parent Fiber	Dry Denier	Tenacity	Elonga- tion	Initial Modulus	TE 1/2	Max. Temp °C	Dry Denier	Tenacity	Elonga- tion	Initial Modulus	TE 1/2			
2232-38-C1	2232-13-A1	306.0	5.7	18.8	129	24.5	1000	247	9.1	2.7	450	14.9			
2232-38-A1	2232-13-A3	321.3	5.9	21.5	127	27.3	1000x2	239	11.4	1.7	580	12.1			
-38-A2							1000x2	241	10.9	1.3	583	12.4			
-39-A3							1000	251	10.7	2.0	506	15.2			
-39-A4							1100	247	10.6	2.3	515	16.1			
-39-A5							1000	246	10.5	2.3	443	16.0			
-39-A6							1050	254	10.7	2.0	533	15.1			
-39-A7							1000	239	8.2	1.7	483	10.7			
-40-A8							1000	255	11.6	2.4	534	17.9			
2232-33-C3	2232-10-F1	413.1	5.0	44.3	71	33.3	850	290.2	10.2	3.0	366	15.5			
-33-C4	-10-F2	201.6	5.3	27.4	79	27.8	800	143.6	12.4	2.6	426	20.0			
-33-B1	-10-F2	413.1	5.0	44.3	71	33.3	800	302.6	8.8	2.4	345	13.7			
-34-A1	-12-G1	282.6	6.6	19.8	96	29.3	900	223.2	9.7	3.0	312	15.7			
-34-A2	-12-G1	282.6	6.6	19.8	96	29.3	850	225.0	9.7	2.0	440	13.7			
-31-A9	-8-B2	473.1	3.3	67.3	46	26.8	800	243.0	9.8	6.4	205	24.8			
-32-B1	-8-B3	350.0	5.6	41.0	70	35.9	800	249.8	9.2	2.7	333	14.1			
-32-B2	-32-B1						950	238.1	9.2	2.3	400	14.0			
-32-B3	-32-B2						800	216.0	9.7	1.7	515	12.7			
-32-B4	-32-B3						850x3	234.0	9.4	2.0	426	13.3			
-32-C1	-8-B3						850	244.0	9.9	3.0	367	17.1			
-32-C2	-32-C1						850*	237.4	11.4	3.3	373	20.6			

Illustrated in Table XIV is the achievement, in some cases, of AF-Y-56 with initial moduli well above 500 gpd. Thus, from one heat-treating study of 1000°C (Code 2232-36-C6B), heat-treated yarn with  $T/E/Mi/TE^{1/2} = 10.6 \text{ gpd}/2.0\%/550 \text{ gpd}/15.0$ , was obtained. Equivalent tenacity levels were obtainable from lower-temperature treatments, but a lower modulus (520 gpd) was obtained with 900°C heat treatment.

As seen also from Table XIV, variations in the final on-the-run temperature, pass multiplicity and tension levels were examined, to produce maximum tenacity and modulus development. A double pass at temperature was found beneficial toward the development of both increased tenacity and modulus. The use of final pass temperatures of 1050°C and 1100°C produced substantial improvement in initial modulus development also, but had negligible effect in tenacity and extensibility, relative to those produced by a final pass temperature of 1000°C.

From Table XIV it can also be seen that for the N.B. 2232-38 yarn series a maximum heat-treated tenacity level of 11.6 g/denier was achieved ( $T/E/Mi/TE^{1/2} = 11.6/2.4/534/17.9$ ) through the use of lower tension (150-g load) and shorter residence times in the final pass, as well as in the preliminary heat-treatment steps. The use of significantly higher loading levels and longer residence times with the same starting yarn in all of the heat-treatment steps produced a marked decrease in tensile properties. This comparison is shown in Table XV.

It is evident from the heat-treatment data obtained on the program, that the AF-Y-56 system is apparently amenable to higher property development at higher heat-treating temperatures within the same framework of prior thermal conditioning. Indeed, up to 1000°C, within the same family of yarns (derived from as-spun yarn No. 2232-12-H1, Table XIV) final initial modulus varies in a rather regular manner with final heat-treatment temperature (cf. Figure 6).

The complete scheme utilized to obtain the 13.3 tenacity yarn is illustrated below:

#### CURRENT HEAT-TREATMENT STRATEGY FOR AF-Y-56

Temperature (°C)	Tension (g)	Res. Time (sec)
200	80	3.8
400	80	3.8
600	300	3.8
800	150	1.9
1000	150	1.9
1000	150	1.9

Total: 17.1

**EFFECT OF HEAT-TREATMENT TENSION/RESIDENCE  
TIME ON FINAL AF-Y-56 PROPERTIES**

36

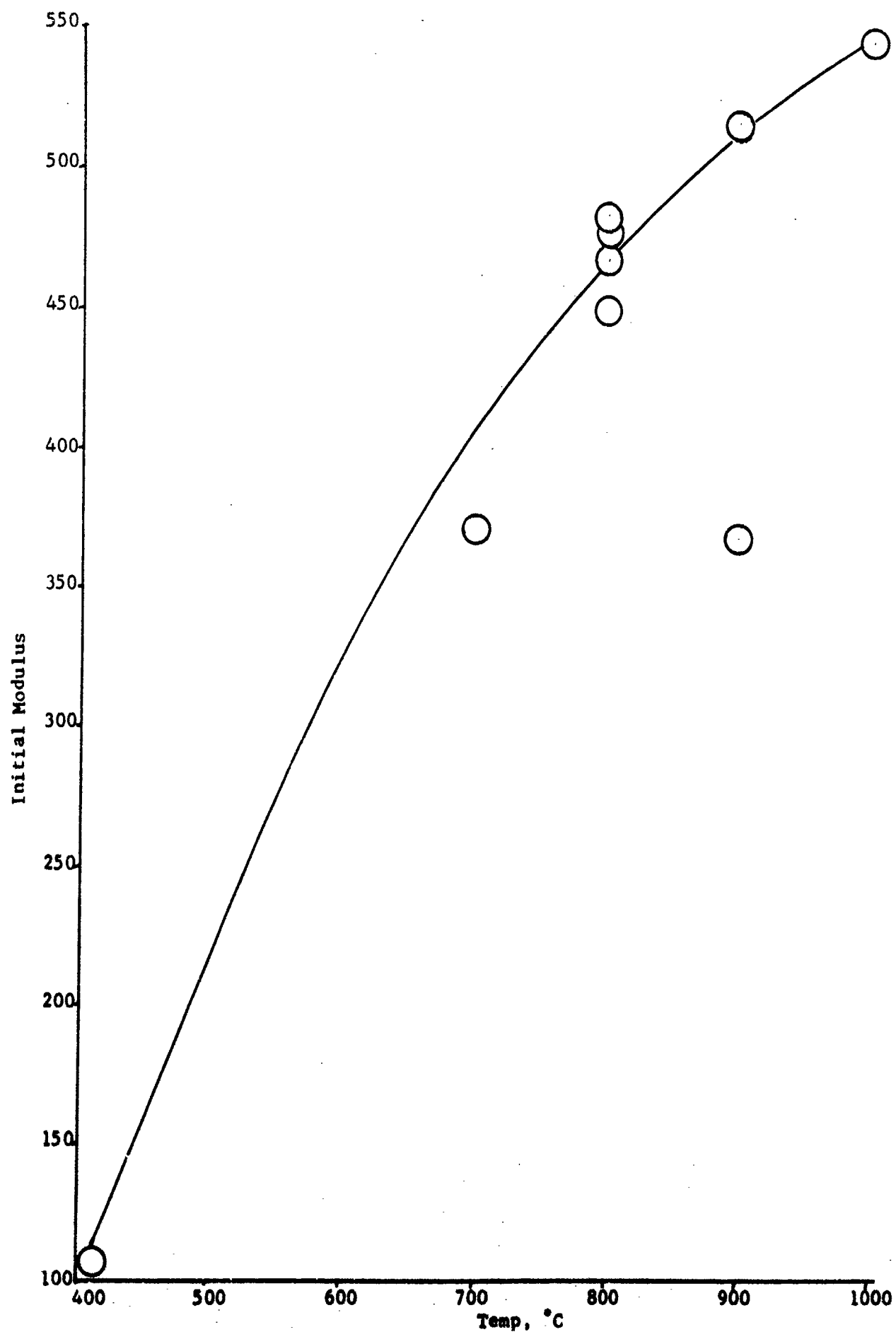


Figure 6. AF-Y-56 Heat-Treated Initial Modulus as a Function of H.T. Temperature

Prior to the advent of the ethyl acetate coagulant system, similar heat treatment studies were carried out using as spun AF-Y-56 coalesced in ether. Representative results are shown in Table XVI.

As seen from this table, yarns with heat-treated tenacities in excess of 10 gpd, and initial moduli in excess of 400 gpd, have been generally obtained. The maximum heat treated tenacity level obtained from ether spinning was 12.3 gpd ( $T/E/M_i = 12.3/2.4/410$ ). The highest heat treated initial modulus obtained with this coagulant system was 457 gpd, at a tensile factor of 18.0, as shown in Table XVI.

What is perhaps most significant about the heat treatment results from ether-spun yarn is the fact that optimum properties were realized with fibers prepared from a spinning solution containing 1.5% solids (the maximum concentration in the table). Indeed, there is a trend toward higher heat-treated tensile properties with increased dissolved polymer concentration, as shown in Table XVI, and also, more clearly in Table XVII. From the data in Table XVI, there is also a similar, but less well-defined trend toward higher as-spun tensile properties with higher dope solids.

Table XVII lists the optimum results obtained at each incremental solids level, abstracted from Table XVI. These data have also been plotted in Figure 7. With the one exception, Fiber -26-A3, which is an exception in a positive sense, there is an essentially linear response of heat treated tenacity to increasing dope solids concentration. Further inspection of the data in Table XVII, as reflected in the heat-treated fiber tensile factor column, offers a possible explanation of the high tenacity level (12.0 gpd) obtained at the 1.4%-solids level. Thus, there is a marked increase in heat-treated tensile factor from the 1.1-1.2% solids level systems to the 1.4% solids and higher systems. There has been observed a parallel increase in the apparent anisotropic behavior of the dopes prepared with solids above 1.4%, relative to that of dopes below 1.4% solids. This difference can be observed visually, and also, more effectively, as birefringence to cross-polarized light.

It thus appears, with ether coagulation that there is a higher degree of solution order at solids concentrations at or above 1.4%, which is translatable to higher perfection fiber, with higher tensile property levels, and to higher tensile factor levels.



TABLE XVI

## AF-Y-56 HEAT-TREATMENT STUDIES FROM ETHYL ETHER COAGULATION

Yarn Code	Percent Yarn	Dope Solids (g)	AS SPUN YARN				Max. Temp (°C)	HEAT TREATED FIBER			
			$V_2/V_1$	Denier	Ten.	Elong.		Denier	Ten.	Elong.	$M_i$
2232-25-B1	2232-2-A1	1.2	2.37	136	4.3	33	825	93	10.4	2.1	431
-25-B2	-2-A4	1.2	1.36	272	2.9	64	800	150	6.8	3.2	234
-26-B3	-2-A2	1.2	1.56	193	3.6	46	825	120	9.8	2.2	423
-26-A2	-4-B1	1.4	1.2	203	3.9	40	825	136	10.9	3.0	392
-26-A3	-4-B2	1.4	1.66	181	4.1	32	800	133	12.0	2.4	418
-27-A4	-4-E3	1.4	1.94	172*	6.1	14	775	128	10.3	2.8	391
-27-A5	-3-E4	1.4	2.11	158*	6.0	12	800	115	10.5	2.4	450
-27-B1	-2-B1	1.1	1.3	209*	4.9	27	775	139	10.3	2.2	463
-27-B2	-2-B2	1.1	1.65	199*	5.2	30	800	121	10.4	3.1	455
-28-C1	-2-A2	1.2	1.6	193	3.6	46	850	117	10.6	1.9	455
-28-C2	-2-A3	1.2	2.65	137	3.5	31	800	87	10.4	2.0	406
-28-C3	-3-B1	1.5	2.27	152	3.7	29	800	102	11.4	2.5	459
-28-C4	-3-B2	1.5	1.77	206	3.3	28	800	137	12.3	2.4	410

\* Dried 45 min @ 140°C

TABLE XVII

CORRELATION OF DOPE SOLIDS WITH HEAT-TREATMENT RESPONSE OF AF-Y-56 (ETHER COAGULATION)

Yarn Code	Z Solids	V <sub>2</sub> /V <sub>1</sub>	AS SPUN			M <sub>1</sub>	Max Temp	HEAT TREATED			N <sub>1</sub>	TE <sup>1/2</sup>
			Denier	Ten.	Elon.			Draw Ratio	Denier	Ten.		
2232-27-B1	1.1	1.34	209.0	4.9	27.0	100	775	1.50	139.0	10.3	463	15.4
-28-C1	1.2	1.56	193.1	3.6	46.2	46	850	1.64	117.5	10.6	455	14.6
-26-A2	1.4	1.20	203.9	3.9	40.4	52	825	1.49	136.9	10.9	392	18.9
-26-A3	1.4	1.66	181.0	4.1	32.0	58	800	1.36	133.0	12.0	418	18.6
-28-C3	1.5	2.27	152.1	3.7	29.0	60	800	1.48	102.7	11.4	459	18.0
-28-C4	1.5	1.77	206.5	3.3	28.2	51	800	1.50	137.9	12.3	410	19.1

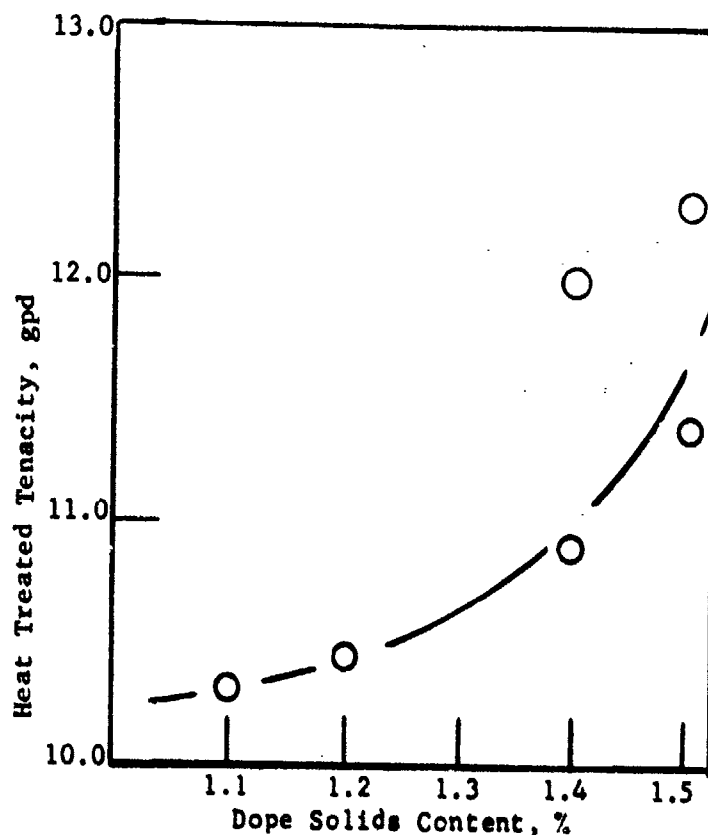


Figure 7. Relationship Between Solids Content and Heat Treated Tenacity of the AF-Y-56 System

Earlier in the program, using 1.0-1.1% solids dopes in formic acid/m-cresol with ether coagulation, an attempt was made to correlate the level of spin stretch, and draw ratio, with the response of the as-spun fiber to tenacity development during high temperature heat treatment. This study is cited in Table XVIII, with the fibers listed in order of increasing spin stretch. From these data the following observations have been made, specifically for these low (1.0-1.1%) solids dopes:

- (1) The percentage increase in tenacity from the as-spun to heat treated state has been found to decrease approximately as a function of the spin stretch value;
- (2) Spin stretch does not, however, seem to materially affect the tenacity level itself of the resulting heat treated fibers;
- (3) The attempted correlation of variation in percentage increase in the absolute failing load, from as-spun to heat-treated fiber with spin stretch, as shown in Table XVIII, appears to only loosely reflect

TABLE XVIII

## CORRELATIONS OF SPIN STRETCH WITH HEAT TREATMENT TENACITY DEVELOPMENT

No.	Yarn Code (Heat Treated) HB 2724-	Polymer Batch	Spin Stretch	Draw		Tenacities		Falling Load, g		Percent Increase
				Temp (°C)	Ratio	As Spun	Heat Treated	As Spun	Heat Treated	
1	47-A6	A	0.43	950	2.44	1.8	7.8	1170	2051	75
2	48-A3	A	0.49	900	2.29	2.2	8.5	1270	2120	67
3	42-A1	B	0.53	800x2	1.71	3.9	8.7	1370	1770	29
4	46-A5	A	0.56	900	2.06	2.6	9.1	1230	2050	67
5	48-A2	A	0.65	875	1.97	2.9	9.8	1200	2050	70
6	48-A3	A	0.65	900	1.90	2.9	8.4	1200	1823	52
7	42-A2	B	0.68	800	1.64	5.2	10.7	1860	2367	27
8	43-A3	C	0.69	750	1.91	3.3	6.7	1360	2220	63
9	44-A2	C	0.69	775	1.30	3.7	10.4	1500	2580	72
10	45-A1	A	0.69	1000	2.15	3.8	8.9	1500	1610	7
11	44-A1	C	0.77	800	1.92	3.8	8.0	2400	2250	-7
12	41-A7	B	0.78	825	3.66	3.6	8.6	2010	1660	-35
13	41-A6	B	0.78	825x2	3.24	3.7	11.0	1800	1660	-8
14	48-B1	A	0.79	850	1.85	3.4	11.3	1200	2190	83
15	46-A6	A	0.80	900	1.91	2.7	8.1	1000	1610	61
16	42-A3	B	0.84	800	1.73	4.5	9.7	1850	2430	31
17	43-C18	B	0.86	800	1.91	4.6	10.0	2070	2380	15
18	43-B2	B	0.87	800	1.79	5.0	10.7	2080	2490	20
19	47-B1	B	0.90	850	1.78	3.0	6.8	1200	1550	29
20	47-B2	B	0.90	900	1.69	3.0	7.8	1160	1800	55
21	43-B3	B	0.92	800	1.68	5.1	10.1	2140	2520	18
22	49-B2	A	1.00	850	1.80	3.3	11.1	1070	1980	85
23	43-B1	B	1.02	800	1.56	5.5	11.3	2420	3170	31
24	40-A3	B	1.07	800	1.78	4.8	8.6	2780	2770	0
25	42-A8	B	1.07	825	1.67	4.0	7.7	2110	1460	-31
26	41-A5	B	1.42	800x2	2.35	4.9	9.0	1440	1130	-22
27	40-A1	B	1.42	800x7	1.69	5.9	9.8	174	173	0
28	37-A4	B	1.99	825	1.17	5.3	6.1	689	671	-3
29	39-B1	B	2.30	800	1.55	6.5	9.9	761	748	-2
30	38-A2	B	2.43	800	1.16	6.4	9.1	1023	996	-3
31	39-A5	B	2.43	800	1.68	6.3	10.2	1006	982	-2
32	38-A3	B	2.43	800x2	1.64	6.3	9.5	1006	1064	6
33	37-B1	B	2.43	850	1.18	5.6	7.7	930	1090	17
34	38-A1	B	2.75	800	1.58	6.3	7.9	891	709	-25
35	39-B2	B	2.91	750	1.30	7.1	10.7	721	829	15
36	30-B1	B	3.06	300	1.70	4.7	6.5	328	266	-19
37	37-A5	B	3.83	825	1.11	6.3	7.0	515	517	0
38	31-B6	B	5.62	475	1.02	5.2	4.8	204	186	-9
39	31-B5	B	5.62	500	1.11	5.8	5.6	252	220	-13
40	30-B4	B	5.62	600	1.11	4.9	6.3	195	224	15
41	31-B7	B	5.62	700	1.02	5.8	6.2	229	237	3

(A) 50-A10 10mh 15.8; (B) 46-B10 10mh 15.2; (C) 39-A6 10mh 16.6 (all in 0.005% H<sub>2</sub>SO<sub>4</sub>)

differences in residual plasticization. Thus the observed larger majority of load increases with spin stretches below 1.0, may merely reflect the need for additional drying of the as-spun fiber.

An attempt has also been made to correlate the draw ratio attained in the heat treatment step with the relative increase in tenacity for that treatment. As shown in Table XVIII, for the 800°C heat treatment, larger percentage increases in tenacity have been obtained with higher draw ratio. These higher draw ratios were in turn obtainable with lower spin stretch levels (i.e., with higher extensibility in the as-spun yarn).

At the more meaningful 2% solids level, a limited statistical survey was carried out, with equivalently prepared yarns, to determine the relationship between spin stretch factor (within the "useful" range of same) and tenacity. All yarns used came from one of three dopes, all at the 2% solids level, prepared identically and spun into ethyl acetate through the same size spinnerets. All yarn samples were treated 1 hr @ 150°C prior to test.

Figure 8, of tenacity vs. spin-stretch factor for each of the three dopes, indicates linear relationships in each case up to a spin stretch level of 1.9. The slopes of two of the three curves are virtually identical. The observed slope variations can readily be attributed to the individual nature of the solutions themselves, and the consequent flow differences. The series of points at a spin stretch of 0.9 show reproducibility to within 10%. In the studies no useful increases in tenacity are in evidence beyond a spin-stretch level of 1.9.

Figure 9 shows the relationship between spin-stretch and as-spun tensile factor for the above-mentioned yarns. As has been consistently observed, the optimum range of spin stretch values for these spins falls between 0.9-1.5.

A limited comparison study was made between the ethyl acetate-coagulated yarn, from a 2% solids dope, and ether-coagulated yarn at the 1.1, 1.4, 1.5 and 2.0% solids level. With an 850°C heat treatment, it was possible to achieve the same heat-treated tenacity for yarns from both coagulant media, at the higher dope solids (2.0% in both cases). These results are summarized below in Table XIX.

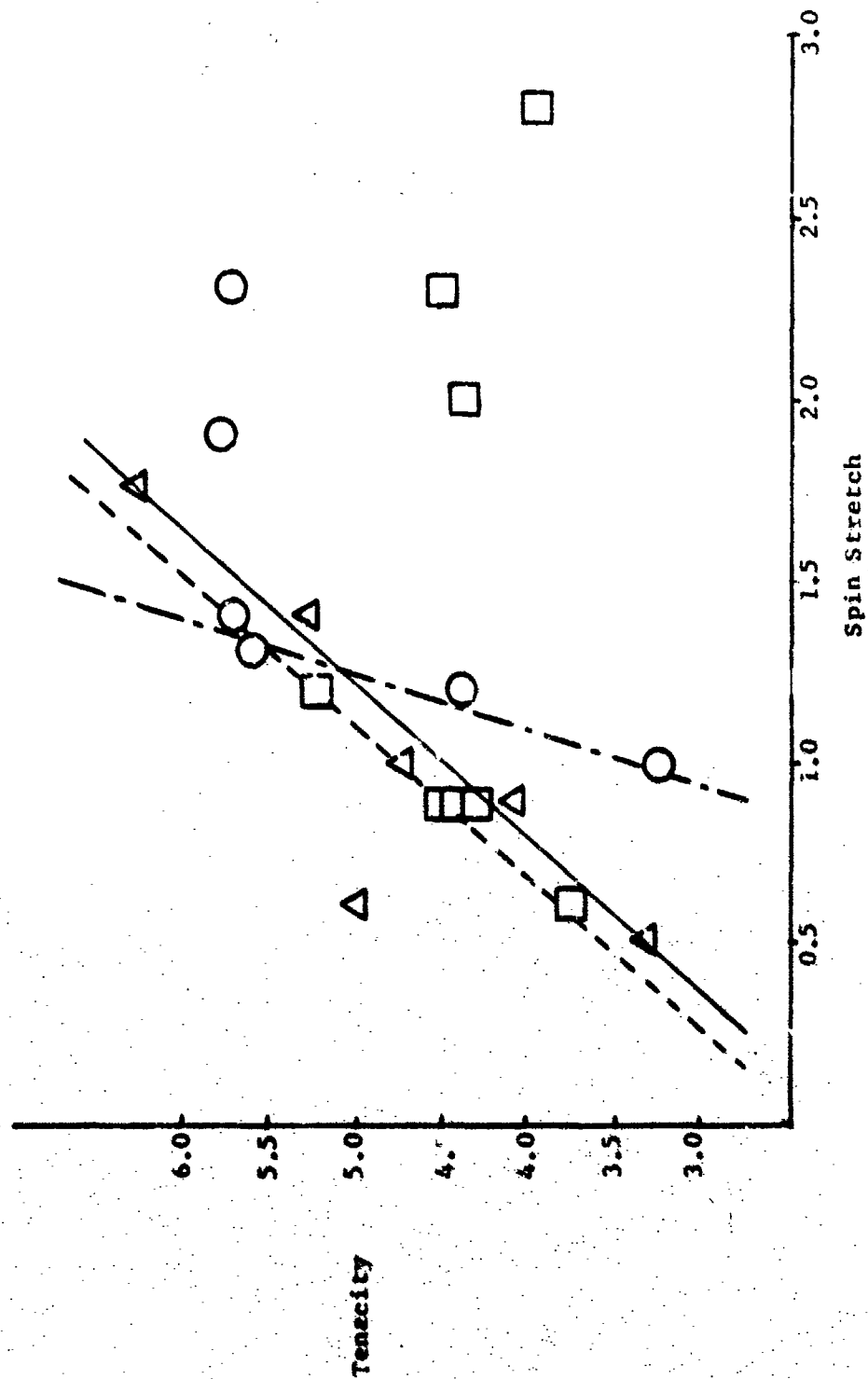


Figure 8. Effect of Spin-Stretch Factor on AF-Y-56 As-Spun Tenacity Utilizing Three Separate Spin Dopes

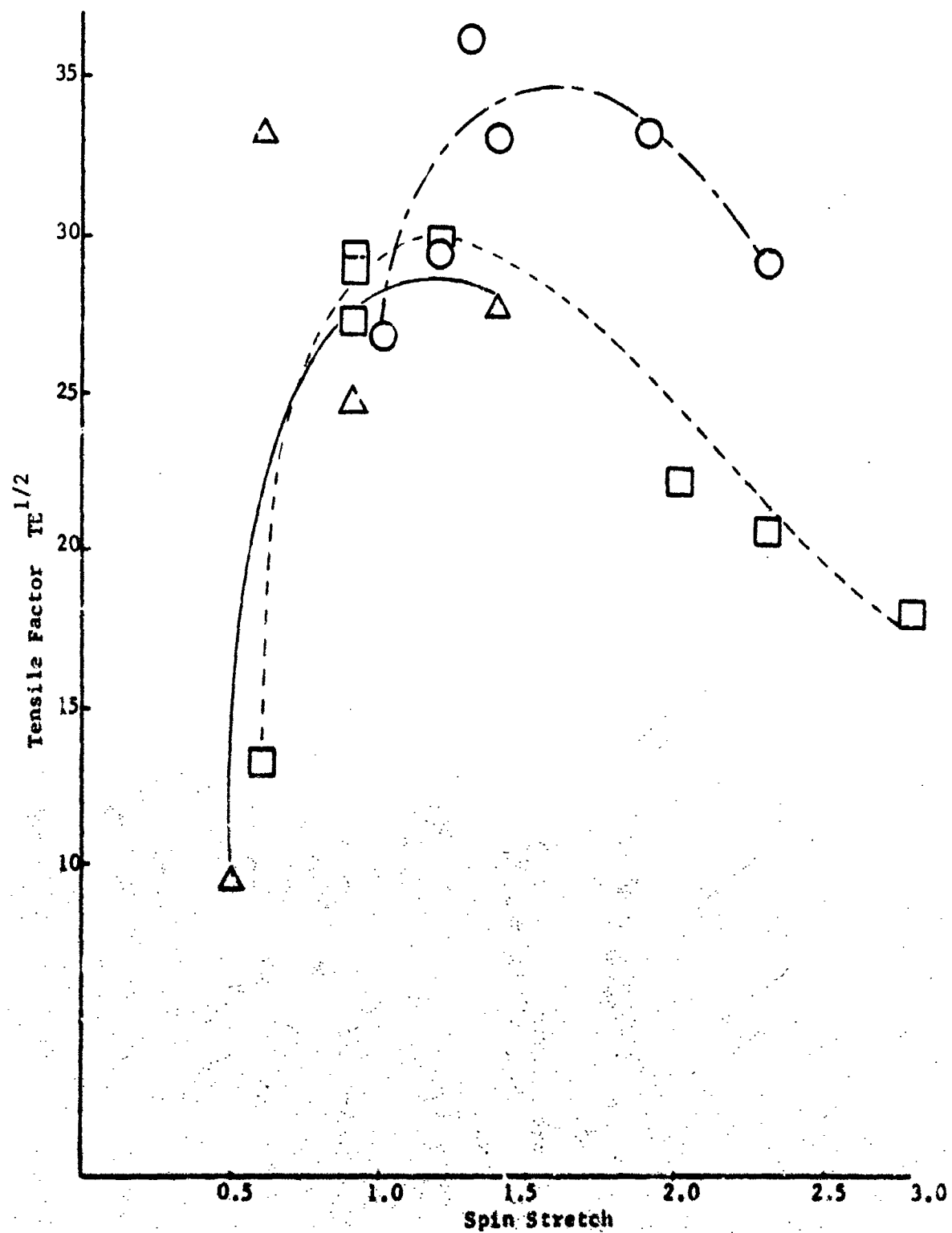


Figure 9. Effect of Spin-Stretch Factor on AF-Y-56 As-Spun Tensile Factor ( $TE^{1/2}$ ) Utilizing Three Separate Spin Dopes

TABLE XIX

COMPARISON OF HEAT TREATMENT RESPONSE OF AS-SPUN AF-Y-56 YARN FROM ETHYL ACETATE AND ETHYL ETHER COAGULATION

AS SPUN YARN										HEAT TREATED YARN				
Hot Stretch Code	Parent Fiber	Fiber History*	Dry Denier	Tenacity	Elonga- tion	Initial Modulus	Max. Temp °C	1/2	Dry Denier	Tenacity	Elonga- tion	Initial Modulus	1/2	
2232-29-C5	2232-4-E3	A	340.2	3.0	47.3	41	800	20.1	210.8	9.0	2.4	357	13.9	
-29-C6	-3-C1	B	216.6	4.2	31.1	55	750	23.2	143.8	6.4	2.3	334	12.7	
-29-C7	-3-C2	B	184.7	3.9	70.4	60	900	17.7	125.7	9.4	2.7	344	15.4	
-29-C8	-3-C3	B	171.9	3.7	21.2	58	800	17.0	119.4	9.7	2.2	343	14.4	
-29-A1	-5-G1	C	108.9	Not Tested			825		70.2	10.1	4.7	285	21.9	
-30-A2	-6-B1	D	65.7	Not Tested			850		90.0	9.9	2.7	422	16.3	
-30-A3	-6-A1	D	364.5	4.6	41.3	45	850	29.5	240.0	11.3	7.0	271	29.8	
-31-A9	2232-8-B2	E	473.1	3.3	67.3	46	800	26.8	243.0	9.8	6.4	205	24.3	
-32-B1	-8-B3	E	350.0	5.6	41.0	70	800	35.9	249.8	8.6	2.7	333	14.1	
-32-B2	-32-B1	E					950		238.1	9.2	2.3	400	14.0	
-32-B3	-32-B2	E					806		216.0	9.7	1.7	515	12.7	
-32-B4	-32-B3	E					850x3		234.0	9.4	2.0	420	13.3	
-32-C1	-8-B3	E					850		244.0	9.9	3.0	367	17.1	
-32-C2	-32-C1	E					850		237.4	11.4	3.3	373	20.6	

\* Fiber History: A) Ether coagulant, 1.4% solids, 105°C drying  
 B) Ether coagulant, 1.5% solids, 105°C drying  
 C) Ether coagulant, 1.0% solids, 105°C drying  
 D) Ether coagulant, 2.0% solids, 105°C drying  
 E) Ethyl acetate coagulant, 2.0% solids, 150°C drying



e. Moisture Regain Studies

A series of moisture regain studies were carried out on both the as-spun AF-Y-56 yarn (cf. Table VI) and also its heat-treated counterpart which had been given a final pass in a 1000°C oven. Representative values obtained are cited in Table XX below. The regain level of heat-treated fiber, while significantly lower than that of as-spun fiber, was nevertheless higher than anticipated.

TABLE XX

MOISTURE REGAIN LEVELS FOR VARIOUS AF-Y-56 MODIFICATIONS\*

<u>Sample Treatment</u>	<u>Ten.</u>	<u>Elong.</u>	<u>Mod.</u>	<u>TE</u> <sup>1/2</sup>	<u>Wt. % Moisture Regain*</u>
As-Spun	4.9	19.0%	107	21.4	33
Heat Treated @ 1000°C	8.9	2.1%	508	14.5	21
" "	8.0	1.7%	501	10.3	28
20-mesh granular polymer $\eta_{inh}$ - 11.0 (0.005%; H <sub>2</sub> SO <sub>4</sub> )	--	--	--	--	28

\* Equilibrated at mean temperature of 72°F @ R.H. = 70-75%.

In general moisture regain levels for as-spun AF-Y-56 yarn span a range of 29-35%, and heat treated yarn, a range of 21-28%.

A comparative moisture regain study was carried out between the production Celanese DAB-DPI Phl (sample supplied by AFML) and the WRD AF-Y-56 system. To remove any surface treatment on the Celanese fiber staple, it was refluxed in a 10% solution of TSP for 1/2 hr then rinsed several times with H<sub>2</sub>O and finally refluxed 1/2 hour in H<sub>2</sub>O prior to drying. The study indicated a 20.2% regain for the Celanese sample and 32.3% for the AF-Y-56.

f. Monofilament Studies (AF-Y-56)\*\*

Prior to the efforts described in this report heretofore a development effort logically preceded the evaluation of the successful system. These efforts occupied approximately the first 1/2 of the time

\*\* Air Force Fiber No. 56 (monofilament)

span of the contract. Solvents investigated prior to uncovering the unusual formic acid/m-cresol system were primarily two:  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$ . Efforts described below are an account of these development efforts and include preliminary attempts with the latter successful formic acid/m-cresol solvent system. These results are compiled in Tables XXI, XXII and XXIII, and discussed individually under each solvent heading below.

1) Formic Acid Spinning Solutions. Initially the discovery that formic acid was a solvent for the A-B PBI system appeared most promising. Dopes with solids as high as 2.1% were prepared from purified polymer of  $\eta_{inh} = 9.7^*$ . Many attempts to wet spin dopes of 1.0 and 1.5% solids into a variety of coagulant media all provided filaments of insufficient strength for threadline maintenance. Coagulants used included water at room temperature and also at  $90^\circ\text{C}$ , ethanol, isopropyl alcohol, methanol, 15% aqueous ammonium hydroxide, 40% sulfuric acid, acetonitrile, ethylene glycol, 25% formic acid, and others. With a 2% dope, however, it was possible to windup useful fiber with isopropyl alcohol or aqueous formic acid (10-25%). The mediocre filament tensile properties ( $T/E = 2.0$  gpd/8.3%, at a denier of 16 obtained with isopropyl alcohol coagulant) did not in any way reflect the high viscosity of the polymer used. Slightly lower properties were obtained with aqueous formic acid as coagulant. With either water or 40% aqueous sulfuric acid, insufficient strength was obtained during coagulation to maintain a threadline. Multifilament spinning efforts with this 2% solids formic acid dope were in every case unsuccessful because of the slow coagulation rate, which produced welding of the individual filaments.

2) Formic Acid/m-cresol Spinning Solutions. The many studies conducted with the formic acid-m-cresol system into varying coagulating media eventually led to diethyl ether and ethyl acetate as the preferred coagulating media. The success of these mediums is described in detail in the preceding yarn section. Attempts with nonaqueous protic coagulant systems, such as alcohols, led to the variable spinning results seen in Table XXI. Thus, two attempts to repeat the fiber spinning initially obtained with isopropyl alcohol as the coagulant, resulted in production of low quality fiber of insufficient strength for testing. The reason for this lack of reproducibility with this coagulant is not clear. It may be related to a general unsuitability of protic coagulants for this polymer from this solvent pair. Dope clarity was not monitored at this point on the program.

### 3) Sulfuric Acid Spinning Solutions.

a) Monofilament. In a single run with 10% solids A-B PBI sulfuric acid solution (polymer  $\eta_{inh} = 3.3^*$ ) several yards of continuous monofilament were collected using an 8-mil spinneret. The conditions employed and the test results on the fiber are given in Table XXII.

\* 0.5%/H<sub>2</sub>SO<sub>4</sub>

TABLE XXI  
AF-F-56 WET-SPINNING STUDIES

Polymer Code; Inherent Viscosity*	Spinning Solvent; % Solids	Spinning Conditions**		Monofilament Tensile Properties			
		First Bath	Second Bath	Denier	Tenacity (gpd)	Elongation (%)	TE <sup>1/2</sup>
02217-9-B7 $\eta_{inh} = 8.1$	Formic Acid/ m-cresol 80/20, 1.0%	iPrOH	None	28.4	2.9	14.0	10.8**
(Two attempted repeats of this spinning produced filaments TWTT)							
2201-27-B1 $\eta_{inh} = 9.7$	Formic acid 1.0%	H <sub>2</sub> O; EtOH; iPrOH; MeOH; 15% NH <sub>4</sub> OH; 40% H <sub>2</sub> SO <sub>4</sub> H <sub>2</sub> O @ 90°C	None	Insufficient strength to maintain threadline			
	Formic acid 1.5%	Acetonitrile; Ethylene glycol; 25% Formic Acid; Others	None	Insufficient strength to maintain threadline			
	Formic acid 2.1%	iPrOH 10% Formic 25% Formic 40% H <sub>2</sub> SO <sub>4</sub> H <sub>2</sub> O	None	16 18 16	2.0 1.5 1.4	8.3 8.8 8.4	5.6 4.3 4.2
				Insufficient strength to maintain threadline			
02217-18B7 $\eta_{inh} = 2.9$	Formic acid/ m-cresol 80/20, 2.5%	iPrOH	None	Insufficient dope viscosity			
02217-9-B7 $\eta_{inh} = 8.1$ and 02217-12-A8 $\eta_{inh} = 8.4$	Formic acid/ m-cresol 80/20, 1.0%	Diethyl ether (5°C)	None	26.0 24.3	0.6 0.4	53 43.2	4.5 2.8
02217-25-B3A $\eta_{inh} = 2.7$	Formic acid/ m-cresol 80/20, 1.3%			TWTT			
02217-9-B7 $\eta_{inh} = 8.1$	Formic acid/ m-cresol 80/20, 0.9%	Ethyl acetate		10.8	1.0	15.0	3.7
02217-4-B9 $\eta_{inh} = 5.3$	96% H <sub>2</sub> SO <sub>4</sub> 1.5%	40% H <sub>2</sub> SO <sub>4</sub>	60° H <sub>2</sub> O	10.2	1.3	12.5	4.3
02217-18-B7 $\eta_{inh} = 2.9$	96% H <sub>2</sub> SO <sub>4</sub> 7.5%	40% H <sub>2</sub> SO <sub>4</sub> iPrOH	60° H <sub>2</sub> O 60° H <sub>2</sub> O	65.9 69.4	1.0 0.7	21.2 11.5	4.4 2.5
02217-18-B7 $\eta_{inh} = 2.9$	99% H <sub>2</sub> SO <sub>4</sub> 5%	40% H <sub>2</sub> SO <sub>4</sub> iPrOH	60° H <sub>2</sub> O None	Too brittle to test TWTT			
02217-4-B9 $\eta_{inh} = 5.4$	100% H <sub>2</sub> SO <sub>4</sub> 1.5%	40% H <sub>2</sub> SO <sub>4</sub> iPrOH	60° H <sub>2</sub> O None	Too brittle to test TWTT			
2201-27-B1 $\eta_{inh} = 9.7$	Sulfuric Acid, 4%	iPrOH iPrOH MeOH EtOH	None 60° H <sub>2</sub> O	60 54 36 30	1.8 2.1 2.2 1.9	29 37 31 32	9.7 12.9 12.1 10.7
	Sulfuric Acid, 7%	iPrOH 40% H <sub>2</sub> SO <sub>4</sub>	60° H <sub>2</sub> O	74 60	1.3 1.3	3.8 8.5	2.5 3.8
1015-14-Q2 $\eta_{inh} = 3.3$	Phosphoric Acid, 10%	40% H <sub>2</sub> SO <sub>4</sub> 90° H <sub>2</sub> O	90° H <sub>2</sub> O None	41 86	Too weak to test 1.7		80 15.6
02217-35-B1 $\eta_{inh} = 7.1$	100% H <sub>3</sub> PO <sub>4</sub> *** (20/8 mil)	70°C H <sub>2</sub> O	None	25.6	0.8	28.0	4.3

\* 0.5% H<sub>2</sub>SO<sub>4</sub>

\*\* Room temperature unless otherwise specified.

\*\*\* Yarn

TABLE XXII

AF-F-56 PROPERTIES FROM  
SULFURIC ACID SPINNING (SPLIT BATH)

Number	Spin-Stretch Ratio	Filament Diameter, mm	As-Spun Filament Properties				
			DPF	T, gpd	E, %	$M_i$ , gpd	$TE^{1/2}$
1	1.0	0.080	49.2	2.7	25	77	13.5
2	1.5	0.062	33.4	3.8	25	91	19.0
3	1.9	0.057	26.3	4.4	10	104	13.9
4	2.3	0.050	21.5	5.8	8	125	16.4
5	2.4	0.050	20.6	6.2	7	125	16.3

Spinning Conditions: 1st Bath: 40 wt %  $H_2SO_4$ , RT, 5 ft in length;  
2nd Bath: Water, 50°C, 4 ft in length,  
Extrusion: 0.20 mm orifice, 1g/min (0.54 cc/min),  
Bobbin: Overnight in water, boiled-off in water  
(1 hr), dried 18 hr @ 110°C

Since the initially-coalesced filament had strength in the 40% sulfuric acid bath without stretching, a single wrap was taken on the first (underwater) bobbin, the speed of which was adjusted to maintain the threadline. The windup bobbin speed was then adjusted to minimum tension, producing a filament with a denier of 49.2. The denier calculated from the extrusion rate, orifice size, and the percent solids of the dope was ca. 52.

Higher spin stretch ratios were then effected by increasing the windup bobbin speed, and filament samples were collected for ratios up to 2.4, producing a linear increase in tenacity and initial modulus, with a corresponding decrease in denier and elongation. Higher stretch ratios were not possible, due to the high complexing ability of the sulfuric acid for this fiber.

It was anticipated that the bath conditions suggesting the best coagulating conditions for the fiber should be determinable by a plot of the bath conditions vs. the tensile factor  $(TE^{1/2})^{(4)}$  of the fibers obtained under the various conditions. This type of plot is shown in Figure 10 below for a wet spun 6-T nylon system by Epstein and Rosenthal.<sup>(5)</sup>

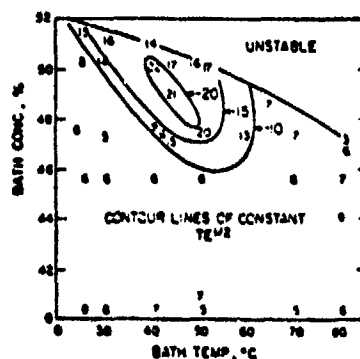


Figure 10. Tensile Factor vs. Coagulation Bath Variables

Results obtained on the studies directed toward optimization of fiber coagulation conditions for the AB-PBI dopes in sulfuric acid are shown in Table XXIII. All of the fibers were monofilament from an 8-mil orifice, spun in the split-bath unit under the conditions stated for the first bath, 50°C water for the second bath. Since  $TE^{1/2}$  maximization was the object of this study, measurements were not made on bath stretch or other variables not pertinent to the calculation of  $TE^{1/2}$ .

Fibers prepared from the 40% sulfuric bath at room temperature were used as control samples. Most significant is the  $TE^{1/2}$  variation between the dopes prepared from the methanol- and the water-precipitated polymers, as is the apparent variation between the 10% and 7.5% dopes from the water precipitated polymer. The reasons for these observed differences are not clear. It appears that the 40% concentration RT conditions are the most suitable for the sulfuric acid AB-PBI coagulation. For optimized spinning solutions which appear to give more predictable  $TE^{1/2}$  values, the study should be repeated.

TABLE XXIII  
EFFECT OF COAGULATION BATH VARIABLES ON TE<sup>1/2</sup> FOR  
AF-F-56 WET SPINNING FROM SULFURIC ACID

Source PPA Polymerized Polymer; Coagulated with	Dope Solids	Conditions of 1st Bath		Fiber Properties	
		Sulfuric Acid Conc., %	Temp, °C	Tenacity, gpd	Elongation, % TE <sup>1/2</sup>
MeOH	10%	40	15	0.8	1.5
		40	RT	1.8	7.3
		40	RT	1.6	8.8
		40	35	1.6	7.9
		40	45	1.3	6.8
		30	RT	1.8	8.8
		30	45	1.4	3.0
		48	RT	1.2	2.6
		60	RT	Too brittle to test	
	10%	40	RT	3.9	8.0
		40	45	2.4	3.7
		38	RT	1.75	56
	7.5%	40	RT	2.9	26
		42	RT	2.5	25
					10.9
					4.6
					13.0
					14.8
					12.5

During the course of investigating the optimum conditions for the spinning of the sulfuric acid AB-PBI dopes, the 7.5% solids AB-PBI dope in sulfuric acid was observed to provide exceptional coagulation, wet strength and transparency as compared to previous sulfuric acid dopes. This superior dope was prepared from an equal mixture of a 5% and a 10% solids dope, neither of which had themselves displayed exceptional behavior during initial spinning coagulation.

The inherent viscosities of the polymers from the two dopes used from the composite dope are shown below.

<u>Dope, % Solids</u>	<u>Inherent Viscosity (0.5% H<sub>2</sub>SO<sub>4</sub>)</u>
10.0	2.8
7.5	2.2
5.0	1.9

These slight variations in inherent viscosities are not considered large enough to explain the observed behavioral differences during coagulation. Ultraviolet spectrophotometry also failed to reveal significant differences in the polymers involved.

The above described effort with sulfuric acid (Table XXII) preceded the eventually successful formic acid/m-cresol solvent system. The preliminary efforts were never repeated successfully to produce a fiber from a protic solvent with a tenacity of 6.2 as shown in Table XXII. More typically, fibers with strengths as seen in Table XXIII were invariably obtained from attempts to duplicate the original sulfuric acid produced fiber.

Similarly disappointing were the results from spinning studies from 99% and 100% sulfuric acid as shown in Table XXI. These dopes, prepared by adding "Sulfan-E" (sulfur trioxide) to 96% sulfuric acid, were designed to assess the effect of the residual water on solubility and spinnability. Very poor fibers resulted from all attempts to spin these dopes. The last system seen in the table did not give the typical AF-F-56 after boil-off. The fibers were treated in water. Apparently the polymer had been sulfonated or partially oxidized (residual amine groups) by SO<sub>3</sub> to change the fiber to dark brown.

In summary it appears that the solvating power of sulfuric acid is too strong to permit reproducible coagulation in aqueous or nonaqueous media. Much additional research for better coagulation is in order to stabilize this system.

b) Multifilament. Based on the spinning coagulation benchmark obtained with monofilament, AF-F-56, obtained from the 40% sulfuric acid (1st bath) - 50°C water (2nd bath) system, a 280-hole, x 3-mil spinneret (Electro-Foil) was used to wet-spin a 7.5% solids dope of  $\eta_{inh} = 3.3^*$  polymer in 96% sulfuric acid. The coagulation conditions proved to be excellent, and lustrous multifilament yarn was wound up at a spin-stretch ratio of 2.2 (filaments transparent throughout the length of passage in both baths), and boiled off on-the-bobbin. The as-spun yarn properties were: tenacity: 3.4 gpd; elongation: 10%; initial modulus: 100 gpd; with a yarn denier of 135, and 0.5 DPF.

4) Phosphoric Acid Spinning Solutions. A spinning solution, at the 10% solids spinning level, was prepared in 85% syrupy phosphoric acid from a polymer of  $\eta_{inh} = 3.3^*$ . This extremely viscous dope was spun (monofilament) into 90° water, yielding a weak filament, with T/E = 1.7 gpd/80%. The  $TE^{1/2}$  value (15.6), as shown in Table XXI, indicates that this dope should be capable of yielding a useful fiber if the dope could be properly processed. An effort to obtain multifilament yarn was unsuccessful, because of high spinneret face pressure, even with high open-area spinnerets and a distribution plate.

As previously discussed the above described spinning attempt apparently was an isolated event since polymer prepared later in the program were found to be invariably insoluble in 85% phosphoric acid.

5) Direct Wet Spinning of AF-F-56 from PPA. Initial attempts to find suitable bath conditions for wet spinning the AF-F-56 directly from PPA showed 90°C water to be ineffective with respect to fiber coagulation. Temperatures above 100°C should be investigated, with compositions such as sulfuric acid-H<sub>2</sub>O, phosphoric acid-H<sub>2</sub>O, glycol-H<sub>2</sub>O to increase the slow coagulation rate observed with the 90°C water. The solution used in these studies was prepared from a 1.6% solids solution of AF-R-56 in PPA (84.7% P<sub>2</sub>O<sub>5</sub>) which had been diluted with 85% phosphoric acid to give 1.0% solids content. Most promising was the RT-viscosity reduction from 10<sup>6</sup> poise to 10<sup>4</sup> poise, effected by the dilution with the phosphoric acid.

#### B. Ordered Aromatic Polybenzimidazole AA-BB-PBI

A lack of useful molecular-weight development was observed in MS-polymerizations directed at a tractable AA-BB PBI polymer using the approach depicted in Figure 11.

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\* 0.5%/H<sub>2</sub>SO<sub>4</sub>



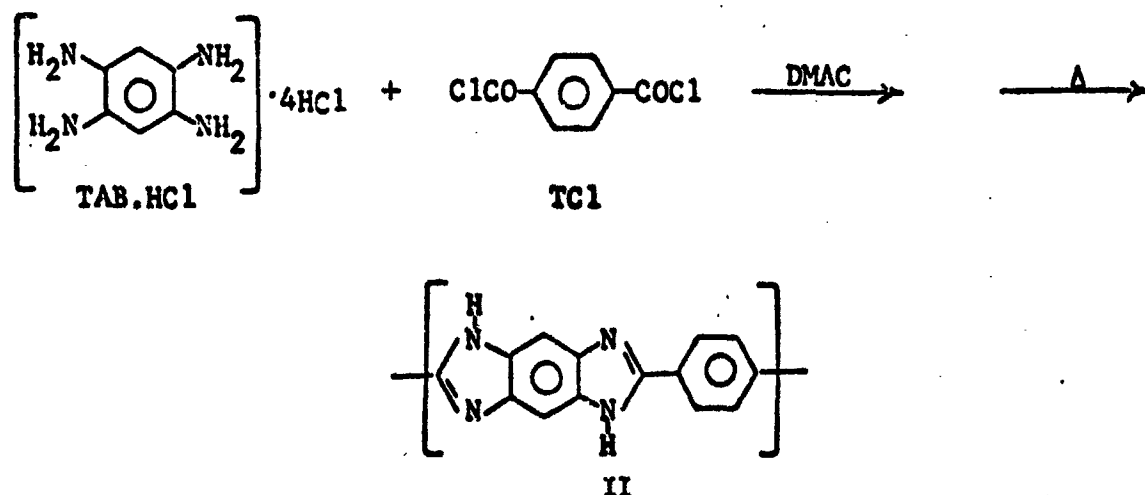


Figure 11. AA-BB PBI Synthesis

Thus, initial syntheses of the ordered AA-BB PBI system by the modified-solution (MS-) polymerization, shown above in Figure 11, produced low molecular weight amino-amide ( $\eta_{inh} = 0.34^*$ ;  $\text{H}_2\text{SO}_4$ ). Efforts to advance and cyclize this product to the PBI using either refluxing acetic anhydride or the potent  $\text{DMF.SO}_3$  reagent gave a product completely insoluble in hot sulfuric and methanesulfonic acids. This insolubility precluded wet spinning studies from these solvents. Similarly, pure thermal treatment at  $400^\circ\text{C}$  under vacuum, of the prepolymer of II produced higher molecular weight product, with concurrent loss of tractability, even in the above mineral acids.

A repeat of this polymerization under more controlled conditions to preserve solubility produced a low molecular weight prepolymer ( $\eta_{inh} = 0.06^*$ ). Subsequent thermal advancement ( $320^\circ\text{C}$ ) produced soluble polymer but of too low a molecular weight ( $\eta_{inh} = 0.16$ ) for film forming or spinning considerations.

A modification of this reaction was carried out in HMPA as the MS-polymerization solvent. This time, however, neutralization of the acidic reaction product with lithium carbonate was effected after the initial reaction period of 40 hours at room temperature (NOTE: the reaction was initiated at  $5^\circ\text{C}$ , by adding solid terephthaloyl chloride to the amine hydrochloride in HMPA). The neutralized amber solution was heated at the reflux temperature of the solvent for 72 hours, with accompanying partial loss of solubility. The solvent was then removed under vacuum, and the residual prepolymer was washed extensively with hot water and solvents to remove all lithium chloride, and was found to be of low molecular weight ( $\eta_{inh} = 0.15$  in MSA). Subsequent solid-state advancement of this prepolymer was effected by gradual heating to  $350^\circ\text{C}$ , followed by isothermal

\*  $0.5\%/\text{H}_2\text{SO}_4$

heating at this temperature for 48 hours. The final polymer retained essential solubility in MSA, but was still of too low molecular weight for film-casting ( $\eta_{inh}$  - 0.2 in MSA). The wet-cast films were not self-supporting, and monofilament spinning experiments from MSA into either hot water or hot, dilute MSA were unsuccessful.

C. Ordered Poly(benzimidazobenzophenanthroline), BBL Ladder Systems

1. Tetraminobenzene Route

Initial efforts with this system were directed toward producing a tractable BBL precursor which could be converted to fiber and not involve the use of sulfuric or methane sulfonic acids. Research proceeded along the lines indicated below. In retrospect it appears that the main difficulty with BBL synthesis by MS-polymerization routes lies in the spurious reactivity and/or purity of the requisite tetraminobenzene (TAB).

Relevant to the purity, commercial tetraminobenzene hydrochloride (TAB.HCl) was rendered into its pale blue state by prolonged drying under high vacuum at  $\sim 100^\circ\text{C}$ . Its neutralization equivalent, however, was essentially unchanged from the value of 77 which had been obtained on the monomer in its pink state (wet). Because of the fundamental importance of TAB to ladder polymer syntheses, further investigations were conducted into methods which could accurately assess the purity of this monomer. These are summarized below.

<u>Method</u>	<u>Equivalent Weight</u>	
	<u>TAB.4HCl Theoretical</u>	<u>Found</u>
1. Potentiometric titration - acidity	71.0	77
2. Potentiometric titration - chloride	71.0	$\sim 50$
3. Diazotization	142.0	289
4. $\text{SeO}_2$ (gravimetric)	148.1	96.8

The above results indicate that either: a) the compound is still impure or has the incorrect structure; or b) side reactions have occurred in all of the attempts. The latter is more logical, due to the inconsistency among the different types of analysis, which indicates the very sensitive nature of the compound. Elemental analysis of the purified product indicated a far higher level of purity, and also a correct structure, than indicated by the reaction-based analyses.

	<u>% C</u>	<u>% H</u>	<u>% N</u>	<u>% Cl</u>	<u>Total</u>
Calculated for $(\text{C}_6\text{H}_4\text{N}_4\text{Cl}_4)$ :	25.37	4.97	19.73	49.93	100.0
Found:	26.06	5.04	19.68	49.08	99.86

Since methods 1, 2 and 4 all showed 3,4-diaminobenzoic acid to be 99+% pure it is surprising that they all fail with the tetraminobenzene. Supplemental efforts directed toward purity determination of this monomer should include anhydrous analytical methods such as the condensation of the tetraminobenzene with benzil.

The approaches investigated toward the goal of producing a soluble BBL precursor in aprotic media are discussed below.

In one case, a modification of the PPA-procedure of Arnold and Van Deusen (6) was briefly investigated to attenuate the cyclization with retention of tractability in other solvents than MSA and sulfuric acid was undertaken. In this modification, employing the dianhydride and TAB, liberated in DMF.SO<sub>3</sub> solvent, as shown in Figure 12, the reaction was terminated after 2-hour isothermal aging at 150°C, following an initial incremental heating from 50°C. The product was of low molecular weight, and exhibited solubility only in MSA, and was not further investigated.

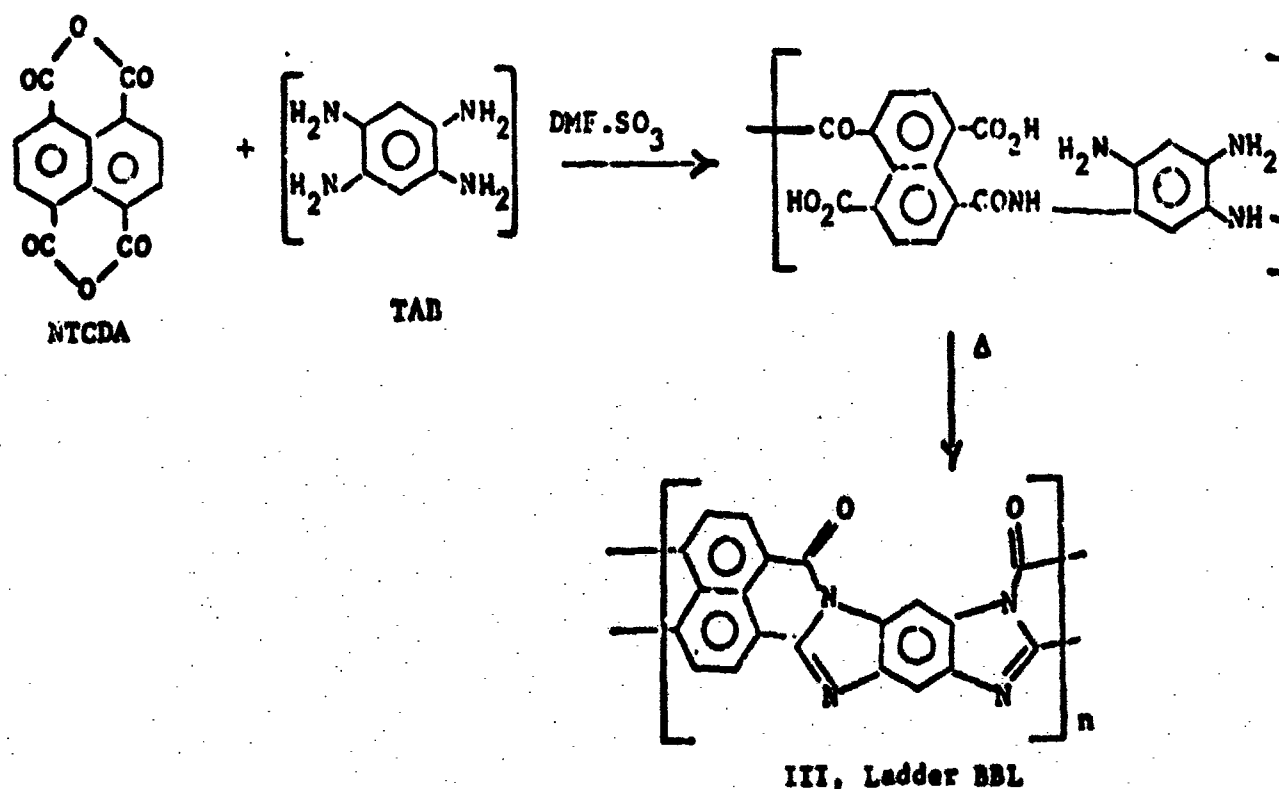


Figure 12. Ordered BBL Synthesis: Anhydride Route

Also MS-polymerization routes, involving gradual release of tetraminobenzene from its hydrochloride in acid-acceptor solvent to produce high molecular-weight tractable precursor to the BBL system, III, as shown in Figure 13, have produced only low-inherent polymer, soluble in MSA. Heating of the neutralized solution ( $\text{Li}_2\text{CO}_3$ ) or the isolated pre-polymer has not shown significant advancement beyond  $\eta_{\text{inh}} = 0.25$ , even after isothermal cycles at  $350^\circ\text{C}$  and  $400^\circ\text{C}$ .

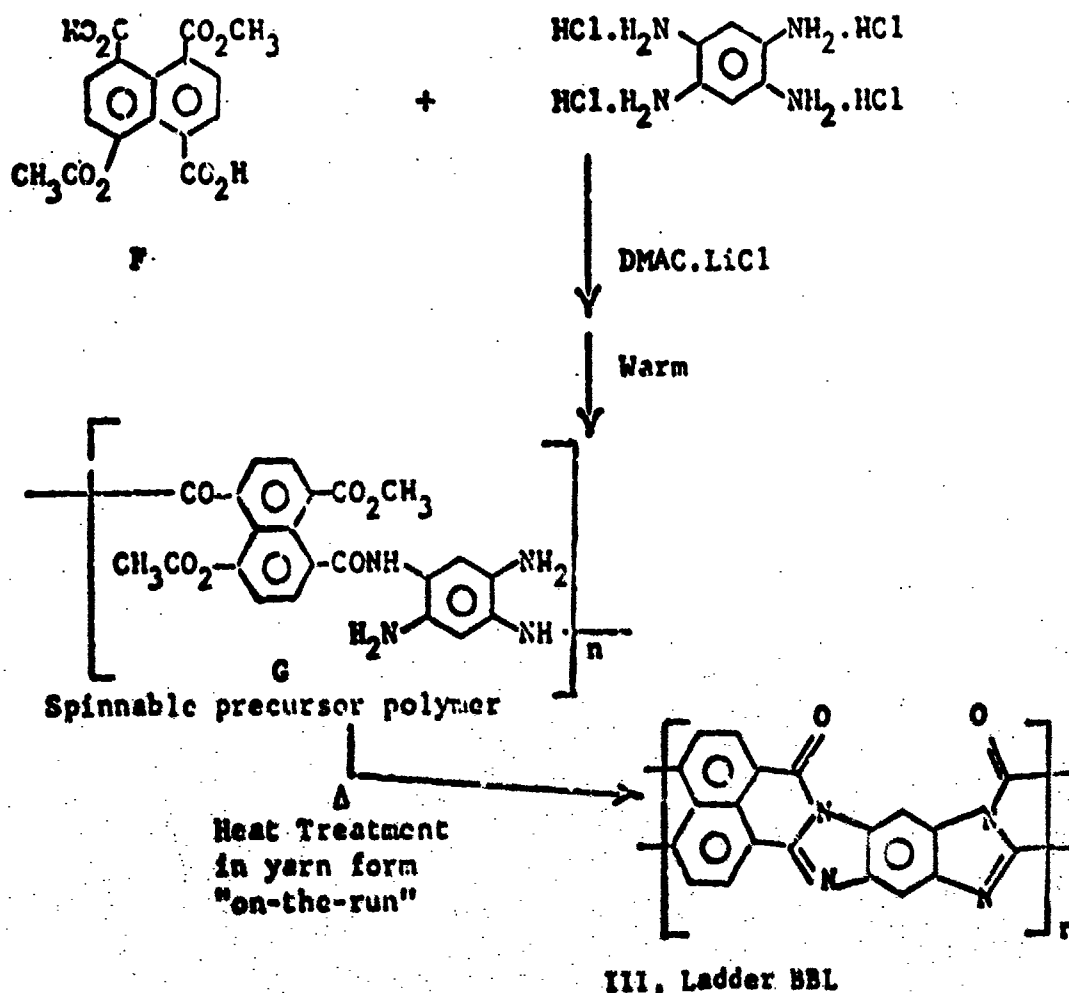
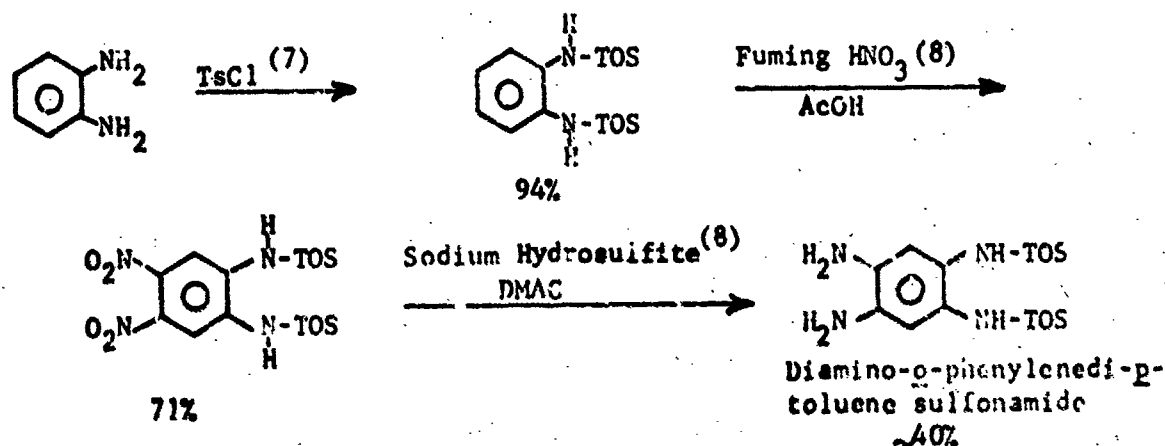


Figure 13. Selective Ester-Acid Route to Ladder BBL

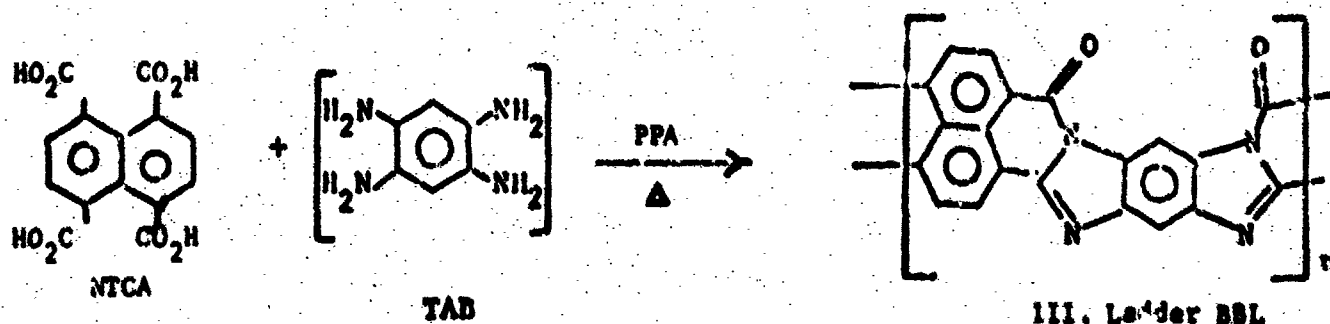
## 2. Derivatized Tetraminobenzene Route

In order to provide for enhanced tetramine oxidative stability, and also a means for monitoring its purity, to yield high molecular weight BBL (and also AA-RB PBI) systems, the di-tosyl derivative of tetraminobenzene was prepared by a modification to the procedure of Cheesman shown below, at the suggestion of Dr. F. E. Arnold of AFML. The last step resulted in a 40% yield as shown below. This purification of the compound to polymer grade and its subsequent polymerization with NTCH were not pursued beyond this juncture due to the emphasis on the AF-R-56.



## 3. BBL Dissolution Studies

All efforts to prepare useful solutions of freeze-dried BBL polymer (Sample No. BBL-SN7), supplied by F. Arnold, in methanesulfonic acid produced only low levels of dissolution, regardless of rate of shear. These studies were conducted to determine the ultimate level of solubility in this solvent. Solubility of this polymer in DMAC/LiCl (6%) has been negligible at temperatures from 25°C to 100°C, regardless of mode of addition or shear rate. This polymer was prepared by the route shown below.



With the recent availability of perfluoromethanesulfonic acid (PMSA),\* attention was directed toward the preparation of useful spinning solutions of the ladder BBL system, analogous to the MSA solubility found by W. H. Gloor of AFML. Using the sample provided by F. Arnold of AFML, it was found possible to dissolve several percent of the BBL in PMSA, to provide a low-viscosity dark red solution by slow stirring. At the 7.2%-solids level, gelation occurred.

#### D. Ladder Pyrnone (Polyimidazopyrrolone) Systems

Analogous approaches to the above BBL studies, designed to prepare the full ladder pyrnone system IV in fabricated form from a tractable precursor, were investigated. The diester-diacid chloride, H, shown in Figure 14, was prepared by treating pyromellitic anhydride first with absolute ethanol, followed by thionyl chloride treatment.<sup>(8,9)</sup> This selective intermediate was reacted with TAB.HCl in DMAC, initially at 5°C to room temperature, over 24 hours, followed by lithium carbonate neutralization. The reaction product solution was then heated at 90°-95°C for 7 hours, as dictated by slow (5°/min) DTA scans, with retention of solubility. Fragile dark amber films were cast from the reaction solution. These films showed a complexity of structure, by infrared analysis, which precluded their further investigation.

For comparison purposes only, the PPA route to this ladder pyrnone, from pyromellitic anhydride and TAB.HCl,<sup>(1)</sup> has also been run, but with isolation after a three-hour cycle at only 150°C. Total intractability was obtained, even in MSA. This route was consequently abandoned.

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\* 3M - "Fluorochemical Acid"

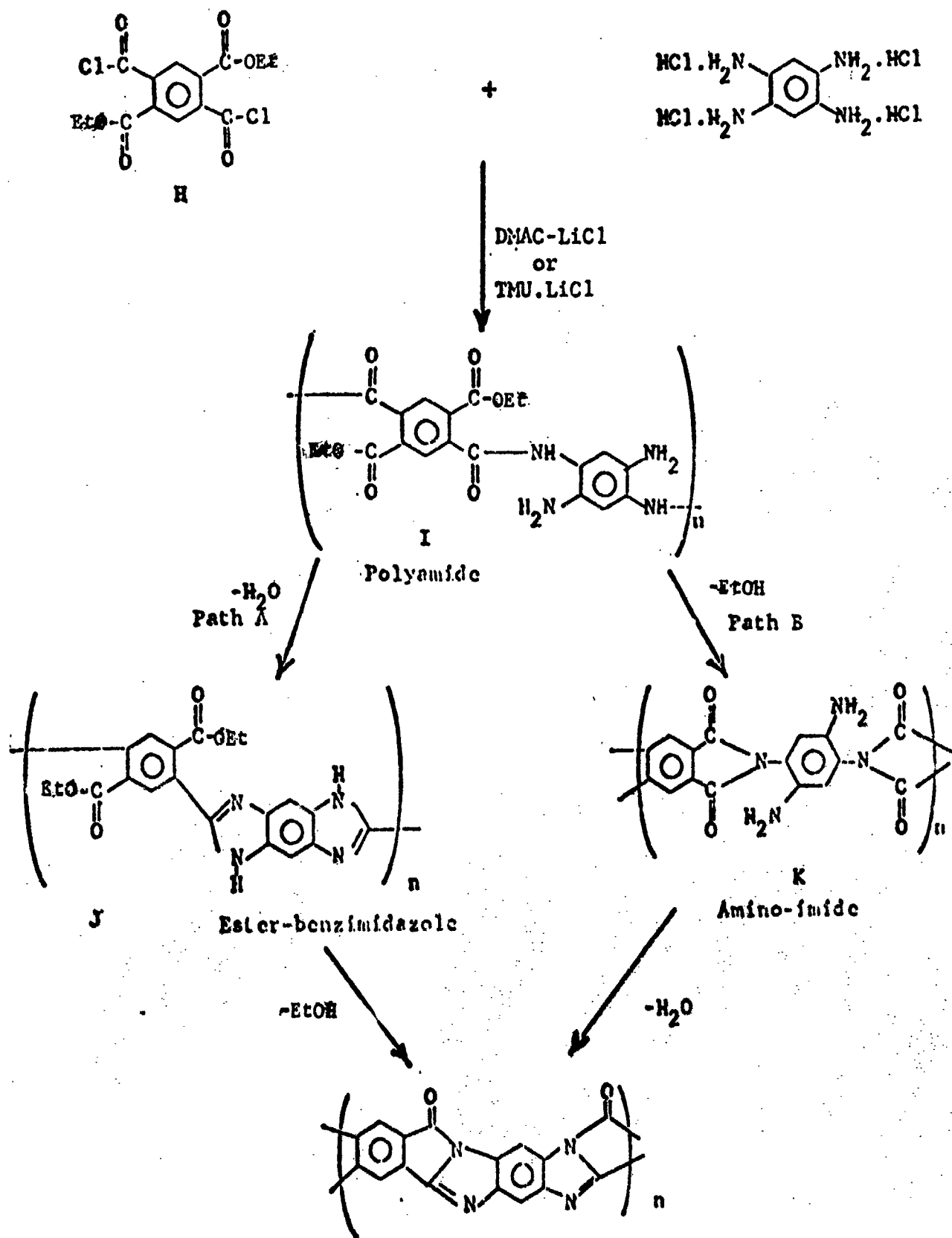


Figure 14. Selective Routes to Ladder Pyrrone

## SECTION II EXPERIMENTAL

### A. Purification of 3,4-Diaminobenzoic Acid (DABA)

DABA is obtained, from Aldrich Chemical Company or American Hoechst Corporation, as a tan powder melting, depending on the lot, in the range of 200° to 208°C (Lit. m.p. 212°C). Careful crystallization from deoxygenated water produced melting point enhancement to as high as 217°C.

(NOTE: It is likely, however, that purity of DABA cannot be accurately assessed by melting behavior, since this acid decarboxylates to o-phenylenediamine immediately at the melting point.)

Attempts were made to back up the melting behavior with DSC analysis and by neutralization equivalent, but no reliably useful differences were found for different purification methods. Likewise, vapor-phase chromatography of the various samples of purified DABA, after silylation with bis-(trimethylsilyl)acetamide, showed only a single major peak, with less than 1% total detectable impurities in all cases.

#### 1. Recrystallization

The following solvents were investigated: dioxane, methanol, methanol-water, ethylene glycol-water, and deoxygenated water. The most successful recrystallization, as determined by m.p. and inherent viscosity development level in pilot polymerizations, was deoxygenated water.

##### a. Recrystallization from Water

To a 12 l 3-necked round bottom flask equipped with heating mantle, nitrogen inlet, stirrer and reflux condenser, was added 10 liter of distilled water. The water was then deoxygenated for 1.5 hour with a nitrogen bubbler. Then 3,4-diaminobenzoic acid (70 g) was added and was dissolved by heating to reflux. To this amber solution was added, 50 g of activated charcoal followed by filtration into a nitrogen-filled flask. The yellow filtrate was treated with 2.5 g of sodium dithionite and allowed to cool slowly. Pink crystals were obtained and collected; recovery: 40%, m.p. 217°C.

#### 2. Acid-Base Purifications

##### a. Sodium Bicarbonate-Acetic Acid

To a solution of 5 g of sodium bicarbonate in 100 ml of distilled water was added 5 g of DABA. After 40 min, the clear amber



solution formed was treated with 5 g of acetic acid added slowly with stirring. The precipitated DABA was allowed to stand in contact with the mother liquor overnight, and then was isolated by filtration. The product was washed with cold water and dried under vacuum; m.p. 204.5°C.

b. Hydrochloric Acid-Sodium Acetate

DABA (15.1 g) in 300 ml of H<sub>2</sub>O with stirring was treated with conc. HCl (8.33 ml). A clear amber solution was formed, which was treated with activated charcoal (3 g) with stirring. After filtration, 14.1 g of sodium acetate was added with vigorous stirring to produce pink crystals of DABA which were isolated as above.

3. Acid Purifications

Both the hydrochloride and the phosphate salts were prepared, but the latter salt failed to polymerize in PPA. The former salt, as prepared below, appears to be nonhygroscopic, stable to air oxidation and unaffected by heating at 110°C for several hours.

a. Hydrochloric Acid-Hydrochloric Acid

To 75.5 g of DABA and 1500 ml of distilled water was added 42 ml of concentrated hydrochloric acid. After 2 hours the clear amber solution was decolorized with 15 g of Norite A. To the clear colorless filtrate was added with stirring concentrated hydrochloric acid (200 ml). The crystals formed were isolated and dried overnight at 110°C.

b. Total Acidity Determination of the DABA.HCl

A weighed sample of DABA.HCl (0.5 g) was dissolved in 100 ml of distilled water. Total acidity was then obtained (-COOH and HCl) by titration with standard 0.1 N sodium hydroxide to a phenolphthalein end point which was verified by potentiometric titration.

Five lots of DABA.HCl have given the following results:

<u>Batch No.</u>	<u>Total Acid (Theory 94.31)</u>
RRD2190-29-2 (Aldrich)	94.5, 94.4
RRD2190-29-1 (Hoechst)	94.8, 94.1
RRD2190-35-1 (Hoechst)	94.4, 94.4
RRD2190-35-2 (Aldrich)	94.1, 94.3
RRD2190-38-1 (Hoechst)	93.98, 93.94

The monohydrochloride salts, obtained as described above were directly polymerized in PPA also. The reaction schedule in each case was: 16 hr @ ~100°C, followed by 4 hr @ 180°C, and finally 3.5 hr @ 220°C. The results are given below.

<u>Monomer Source</u>	<u>H<sub>2</sub>SO<sub>4</sub> Characterization (0.5% solids)</u>		
	<u>Insolubles</u>	<u><math>\eta_{inh}</math></u>	<u>Color of Solution</u>
RRD2190-29-2 (Aldrich)	<0.1%	1.19	Yellow to brown
RRD2190-29-1 (Hoechst)	None	2.50	Yellow

Monomer purity dependency is suggested by the results of these polymerizations.

#### 4. Thin Layer Chromatography of DABA

Hoechst and Aldrich DABA, both as-received and also water-recrystallized, along with water recrystallized p-aminobenzoic acid and m-phenylenediamine were run on an Eastman Kodak TLC plate (6060 Silica Gel w/Fluorescent Indicator) with ethanol as carrier solvent. Results indicated a faint spot over the Hoechst samples (both crude and purified) with the same  $R_f$  as para-aminobenzoic acid. The experiment was repeated using ethanol-acetic acid as a carrier solvent, and provided similar results.

#### B. Optimized Preparation and Purification Procedure for PPA-Prepared A-B PBI

Based on results treated in the foregoing sections, the following preparation-purification scheme has been finalized for pure, high-molecular weight A-B PBI:

- 1) Prepare a 2.0%-solids solution of 3,4-diaminobenzoic acid hydrochloride in 83.05% polyphosphoric acid in resin kettle; and insert in heated oven.
- 2) Conduct the polymerization according to the following schedule; without stirring:
  - 1) 2 hr @ 180°C;
  - 2) 4 hr @ 200°C;
  - 3) 18 hr @ 220°C.
- 3) Precipitate the polymer while still hot in a blender using water.
- 4) Filter, and then extract precipitated polymer with boiling water for 72 hr, changing the water each day.
- 5) Filter and then extract with a threefold volume to polymer volume of concentrated ammonium hydroxide for 16 hr (overnight).

- 6) Filter, wash to neutrality, and re-extract with fresh  $\text{NH}_4\text{OH}$  for 8-16 hr.
- 7) Filter, wash to neutrality, and render essentially dry at  $110^\circ\text{C}$ .
- 8) Store as is for subsequent dissolution.

This procedure was followed to prepare larger quantities of the A-B PBI system for spinning scale-up, as discussed below.

1. Molecular Weight Control by the Incremental Addition of Benzoic Acid to 3,4-Diaminobenzoic Acid in PPA

To a 5-liter, 3-necked flask was added 2000 grams of polyphosphoric acid (83.3% PPA content). The flask and contents were heated to  $100^\circ\text{C}$  and 40 grams (0.212 mole) of 3,4-diaminobenzoic acid hydrochloride (Neutral Equivalent = 94.0) was added portionwise as the rate of  $\text{HCl}$  evolution dictated. The reaction was then continued at  $100^\circ\text{C}$  until it became homogeneous (~24 hours). The calculated weight of monomer and PPA at this point was 2032.2 grams.

A portion of the reaction product mixture (250 g) was poured into a 1 liter test tube with provision for a nitrogen atmosphere. To the remainder of the original monomer-PPA polymerization solution was added 0.0484 grams ( $3.94 \times 10^{-4}$  mole) of Primary Standard benzoic acid. This addition was accomplished quantitatively by weighing of the benzoic acid on a small piece of transfer paper and washing it carefully down a long stemmed funnel onto the surface of the slowly stirred reaction mixture with a few milliliters of cyclohexane. Slow stirring was continued for 1-2 hours until the benzoic acid could no longer be seen, at which time the stirring rate was slowly increased. A 510-gram sample of the new reaction product mixture was then removed and set aside as described above.

The degree of polymerization was then calculated from the moles of monomer remaining in the flask at the time of the benzoic acid addition (0.1854 moles of monomer) to give a calculated D.P. of 468 from which the molecular weight of an idealized polymer structure can be calculated, 71,200. (NOTE: This calculation also requires an assumption that the polymerization will give a polymer of infinite or extremely high molecular weight from the monomer alone.)

Two subsequent additions of benzoic acid were carried out (0.0645 g each) and similar 510-gram samples removed and set aside as described above. The contents of the flask at the end of this procedure weighed 241 grams. The calculated weight which should have been found was 246 grams suggesting only minimal handling losses.

The four test tubes then containing monomer and benzoic acid were placed into a 180°C oil bath for 2 hours. This thermal treatment was followed by 4 hours at 200°C and 23 hours at 215°C. At this point, ca. 1/2 of the contents of each test tube was removed for standard work-up and the remainder was treated for an additional 4 hours at 240°C. The control reaction at this temperature was no longer pourable and had to be spooned from the test tube while that from the last benzoic acid addition had a solution viscosity of ca. 500 poise.

C. Determination of P<sub>2</sub>O<sub>5</sub> Content of PPA

To investigate the influence of the phosphorus pentoxide concentration of the PPA on the polymerization, the guidelines described by Downing and Pearson<sup>(10)</sup> were followed. The best method found by these investigators to monitor the P<sub>2</sub>O<sub>5</sub> content of the PPA was to measure the index of refraction of the PPA. This method gave accuracy to ±0.5%. The following procedure serves as an example of a preparation of PPA with a P<sub>2</sub>O<sub>5</sub> content of 80%.

Into a 1000 ml 3-necked, round bottom flask fitted with N<sub>2</sub> inlet, stirrer, heating mantle and thermometer, was introduced 128.6 g of P<sub>2</sub>O<sub>5</sub> then 100 g of 85% phosphoric acid was slowly added with stirring. (NOTE: It is necessary to add the H<sub>3</sub>PO<sub>4</sub> slowly, as the reaction is very exothermic.) The temperature was adjusted to 120°C and stirring was maintained for 24 hours, to produce a homogeneous PPA solution;  $n_D^{25}$ : 1.4649, corresponding to 79.75% P<sub>2</sub>O<sub>5</sub> content.

D. Preparation of AA-BB Polybenzimidazole from Tetraminobenzene Tetrahydrochloride and Terephthaloyl Chloride

1. Into a 25- ml 3-necked flask, previously purged with nitrogen, were introduced at RT 44 g of DMAC which had been dried, distilled and deoxygenated by bubbling nitrogen through 50°C for 4 hours and 5.68 g (0.02 mole) of tetraminobenzene tetrahydrochloride. To the mixture was slowly added a solution of 4.06 g (0.02 mole) of terephthaloyl chloride, which had been purified by sublimation and subsequent recrystallization from hexane, in 44 g of DMAC. The viscosity increased drastically toward end of addition. The mixture was heated for 3 hours at 70°C (sample of polymer isolated had  $\eta_{inh}$  of 0.34, DMAC). The solution was neutralized with 4.44 g of lithium carbonate and mixture heated at 100°C for 24 hours to attempt ring closure. The dark material was insoluble in H<sub>2</sub>SO<sub>4</sub>.

2. Preparation of AA-BB PBI by adding a mixture of TAB.4HCl and TCl to DMAC resulted in a gel which could not be broken by further addition of DMAC. The isolated polymer was not soluble in sulfuric acid.

E. Preparation of AA-BB PBI from Tetraaminobenzene Tetrahydrochloride and Diphenyl Bibenzoate

Into a 100-ml, 3-necked flask equipped with nitrogen purge were introduced 3.94 g of biphenylbibenzoate (0.01 mole), 2.86 g (0.01 mole) of tetraaminobenzene tetrahydrochloride and 75 ml of dimethyl formamide-sulfur trioxide (DMF.SO<sub>3</sub>) reagent. The mixture was heated to 100°C for 16 hours. It turned from an initially gray heterogeneous mixture to a blue homogeneous solution. The mixture was worked up in water and a cream-colored solid product obtained, which was heated to 375°C to ensure ring closure. A dark product insoluble in H<sub>2</sub>SO<sub>4</sub> and MSA was obtained.

F. Preparation of Ladder BBL

1. Diacid Diester Route. Into a 250 ml, 3-necked flask equipped with nitrogen purge were introduced 50 ml of DMAC and 3.32 g (0.02 mole) of dimethyl ester of naphthalene tetracarboxylic acid. The solution was cooled to 5°C and 2.84 g of tetraaminobenzene tetrahydrochloride were added with stirring. The mixture was stirred 12 hours at 0°C, 12 hours at RT, and 96 hours at 75°C. The solution turned from a initially heterogeneous blue mixture to a purple solution. The solution was neutralized with 8.8 g of lithium carbonate and subsequently heated at 100°C for 8 hours. The polymer was precipitated from water, and dried. The inherent viscosity in methane-sulfonic acid was only 0.25. Heating at 350°C for 4 hours and at 400°C for four hours resulted in polymer with  $\eta_{inh}$  of 0.28 in MSA.

2. Anhydride Route in DMF-SO<sub>3</sub>. Into a 250-ml, 3-necked flask equipped with nitrogen purge were introduced 75 ml of DMF.SO<sub>3</sub>, 2.84 g of tetraaminobenzene tetrahydrochloride and 2.68 grams of naphthalene dianhydride. The mixture was heated at 100°C for 16 hours. It was then cooled and filtered. No solid material obtained. The solution was worked up in water to provide a dark powder, which was subsequently heated at 150°C for 2 hours. It was insoluble in sulfuric acid.

G. Preparation of Ladder Pyrroza

Into a 250 ml, 3-necked flask equipped with nitrogen purge were introduced 100 ml of dimethylacetamide and 3.47 g of diester diacid chloride of pyromellitic acid (prepared by refluxing PMDA in ethanol, isolating diacid diester and subsequently treating with thionyl chloride as per Bell and Jewell.<sup>(9)</sup> The solution was cooled to 5°C and 2.84 grams of tetraaminobenzene tetrahydrochloride were added. The mixture was allowed to come to room temperature during 2 hours and reacted at room temperature for 24 hours. The solution was neutralized with 4.44 grams of lithium carbonate and heated to 90°-95°C for 7 hours. Very fragile dark amber films prepared.

(NOTE: The PPA route from pyromellitic dianhydride and tetraaminobenzene tetrahydrochloride resulted in a completely insoluble gelled product after 3 hours reaction at 150°C. It was insoluble in H<sub>2</sub>SO<sub>4</sub> and MSA.)

## H. Miscellaneous Intermediate Syntheses

### 1. 1,2-Di(p-toluenesulfamido)benzene

10.8 g of *o*-phenylene diamine (0.1 mole) was dissolved in 400 ml of pyridine and the solution was cooled to below 15°C. To this chilled solution was added, portionwise, 38.1 g (0.2<sup>1</sup> mole) of p-toluenesulfonyl chloride over an hours duration. The solution was then allowed to stand at room temperature for a further hour. The product was isolated by pouring the solution over 1 l of cracked ice and adding a further 400 ml of H<sub>2</sub>O, followed by filtration, once the ice had melted. Recrystallization from MeOH-H<sub>2</sub>O, 3:1, gave 39.4 g of pale pink crystals, mp 210.5°-211°C (literature mp 208°C),<sup>(7)</sup> a 94% yield.

### 2. 1,2-Dinitro-4,5-di(p-toluenesulfamido)benzene

To 250 ml of glacial acetic acid was added 32 g of 1,2-di(p-toluenesulfamido)benzene and the suspension was warmed to 60°C. A solution of 7 ml of fuming nitric acid (d. 1.60) in 8 ml of acetic acid was placed in a dropping funnel. One-third of this solution was added rapidly and the remaining two-thirds dropwise. After completion of the addition, the solution was stirred for a further hour and then cooled.

The crude product was isolated by filtration and recrystallized from acetic acid to give 27.9 g of fine yellow needles, mp 249°-253°C (literature mp 251°C), a 71% yield.

### 3. 1,2-Diamino-4,5-di-(p-tolylsulfamido)benzene

A 500 ml, 3-necked flask was charged with 15.2 g (0.030 mol) of 1,2-dinitro-4,5-di(p-tolylsulfamido)benzene and 150 ml of N,N-dimethyl acetamide (DMAC). The flask was fitted with a mechanical stirrer, thermometer, nitrogen inlet and addition funnel containing 31.3 g of sodium hydrosulfite in 170 ml of deoxygenated distilled water. The temperature of the DMAC-solution was brought up to 90°C and held there while the aqueous hydrosulfite solution was added dropwise. As the solution did not turn colorless, 32 g of sodium hydrosulfite in 20 ml of additional water was added and the solution allowed to stir overnight.

Workup of the deep red solution by pouring it into 400 ml of deoxygenated water gave a brown oil. The water was decanted off the oil and it was taken up in tetrahydrofuran and acidified with 2 ml of HCl. The precipitate from the acidification was filtered, washed with ether and dried to give 5.9 g of a pale pink solid, mp 155°C, believed to be 1,2-diammonium-4,5-di(p-tolylsulfamido)benzene dichloride.

The salt does not appear to be soluble in water but appears to go readily into methanol or 50:50 methanol:water (eq. wt. determination failed when analytical lab failed to get material into solution in the same solvents).

Acidification of this salt produced a deep brown solution which upon concentration of the solvent under nitrogen slowly produced a straw-colored crystalline compound, unstable to air (O<sub>2</sub>). An elemental analysis of the compound indicates that it may be a hydrate of the desired product.

4. 1,5-Dichloro-2,4-dinitrobenzene

Nitration of 1,3-dichlorobenzene as per the method of Boyer and Buroks<sup>(11)</sup> gave the title compound in 75% yield, mp 103.5°-105°C, literature mp 103°-104°C.

5. 1,5-Dinitro-2,4-Diaminobenzene<sup>(11)</sup>

A 2 l, three-necked flask was charged with 1 l of nitrobenzene, 121.6 g (0.512 mole) of 1,5-dichloro-2,4-dinitrobenzene, and 78.0 g (1.01 mole) of NH<sub>4</sub>OAc. The solution was heated under reflux in an ammonia atmosphere for 72 hours. Yield of the dinitro compound after filtration from the solvent and subsequent washes with boiling water and boiling ethanol was 61.7 g, mp 304°-308°C, a 61% yield.

For two subsequent preparations ethylene glycol was substituted for nitrobenzene, no ammonium acetate was used and the ammonia was bubbled through the solution. Heating of the solution was limited to 4.5 hours on the first and 12 hours on the second. Both gave comparable yields to the above method but the material after washing and drying was darker in color and melted lower. Combustion analyses indicated no chlorine was present.

### SECTION III RECOMMENDATIONS AND CONCLUSIONS

1. It is concluded that AF-R\*-56 possesses the necessary molecular configuration (backbone linearity) to produce ordered solutions. Evidence for solution order is provided by the similarity of the polymer solutions of the AF-R-56 to liquid crystal behavior and to the realization of high as-spun tenacities (7 gpd) from these solutions.
2. It was observed that the highest tenacities of the as-spun yarn occurred at low spin stretches in the range of 1 to 2.
3. Several attempts with varying coagulants for the preferred polymer solvent (a mixture of formic acid and m-cresol) led to the preliminary conclusion that oxygenated aprotic solvents such as diethyl ether and ethyl acetate are unique in their coagulating ability for this solvent/polymer system.
4. The use of strong acids such as sulfuric or phosphoric as a spin solvent for the AF-R-56 may be possible but will require further efforts to duplicate the quality of yarn produced from the formic acid/m-cresol/ethyl acetate or diethyl ether system.
5. The moisture regain observed for both the as-spun and hot drawn yarns are surprisingly high (30% and 20% respectively). Further research is indicated in this area in order to understand whether these values are due to the nature of the polymer, the spinning conditions, unperfected fiber, or other causes.
6. Heat treating of the AF-Y\*\*-56 with present methods leads to an increase in the tenacity. Doubling of the as-spun tenacities were usually observed with appropriate heat treating schemes, however, with further effort even higher tenacities than the program high of 13 gpd should be attained.
7. The A-BB PBI system based on tetraminobenzene and terephthalic acid due to its apparent backbone linearity is worthy of continued research, even though possibly more intractable than the AF-R-56.

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\* R = Resin

\*\* Y = Yarn



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13. ABSTRACT <p>The subject program has been concerned with the synthesis of specifically ordered heterocyclic polymer systems for evaluation as high tenacity fiber candidates. Specifically sought in the performance spectrum of successful fibers was a high level of mechanical properties, high energy absorption (work-to-break) and high temperature performance. The primary structural criteria for polymer order are: chain growth which describes a straight line; the absence of bulky pendant groups; capability for approaching a planar structure and interchain bonding. These structural features, which are primarily responsible for providing enhanced thermal and mechanical capability relative to non-oriented counterparts, at the same time render the polymer system highly intractable. Hence, specialized solvent systems and dissolution techniques are required for wet spinnability. The AF-Y-56 fiber has been generated by homopolymerization of 3,4-diaminobenzoic acid hydrochloride in polyphosphoric acid. The A-B polybenzimidazole has been obtained with inherent viscosities as high as 17.1 in sulfuric acid, reflecting an agglomerate macrostructure in solution. The polymer has displayed sufficient solubility in formic acid/m-cresol (80/20) for continuous multifilament wet spinning, with ethyl acetate as the preferred coagulant. The as-spun AF-Y-56 yarn, after 300°C drying has displayed tensile properties as high as: tenacity/elongation/initial modulus = 7.4 gpd/30%/97 gpd, with a tensile factor <math>TE^{1/2} = 40</math>, at a dpf = 0.5. This as-spun fiber displayed a moisture regain of ca. 25% at 70% RH. A variety of heat-treatment schemes have been preliminarily investigated with the AF-Y-56 fiber to impart orientation and/or crystallization. Best results to date have been obtained with an on-the-run step drawing series, with a</p> <p style="text-align: right;">(Abstract continued)</p>			

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ABSTRACT (Continued)

final exposure to 1000°-1050°C, with brief exposure. Such heat treatment has produced yarn with  $T/E/Mi = 13/2.2/501$ , with  $TE^{1/2} = 20$ . Initial modulus levels as high as 550 gpd have been obtained by such a strategy, by slight variation in time/temperature/tension. Such heat-treated AF-Y-56 yarn retained ca. 77% of RT-tenacity at 600°F ca. 53% at 700°F, and ca. 47% at 750°F, in initial testing. Attempts were also made to prepare useful spinning solutions of the ladder BBL polymer system, derived from naphthalene tetracarboxylic acid (or its anhydride) and tetraminobenzene. Controlled condensation routes in dipolar aprotic solvents produced only low molecular weight polymer which did not produce useful fiber. Higher molecular weight BBL polymer, prepared in PPA, was found to be soluble to several percent in perfluoromethanesulfonic acid, but no useful fiber was produced in initial small-scale spinning studies.